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A METHOD FOR THE QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF THE ISOTOPIC COMPOSITION OF HEAVY WATER

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Until recently, the basic method used for quantitative analysis of the isotopic composition of water, judging by published results [1, 2], is the mass-spectrometric method. Other methods are also in use, e.g., the refractometric and densitometric methods. Little attention has been given to spectrographic methods for quantitative analysis of the isotopic composition of water. The aim of the work described here, which was carried out in 1952, was development of a method of spectrographic-emission quantitative analysis of the isotopic composition of small samples of water.

Without dwelling in the present instance on general questions of isotopic spectrographic analysis, which have been considered previously [3, 4], we shall briefly describe the method we have developed and the results obtained by means of it.

1. Apparatus for Spectrographic Analysis

A three-prism glass spectrograph, the ISP-51, with an autocollimating camera (F = 1300 mm) was used for resolving the spectrum lines of hydrogen and deuterium. The dispersion of the apparatus at 6500 A, where the analytical lines are located, was equal to 9.5 A/mm. The slit width of the spectrograph was chosen as 30μ. In order to get different grades of blackening, a three step attenuator with transmissions of 100, 29.0 and 10.0% respectively was fitted on the slit.

The spectra were excited with a nonelectrode discharge, supplied by a high-frequency generator [5]. The generator power was 300 watts, with a voltage of 3 kilovolts at a frequency of 10 megacycles. A vacuum apparatus shown in Fig. 1 was assembled in order to get a discharge in water vapor. This apparatus consists of the following parts: a vacuum pump 1, a ballast chamber 2, a manometric tube (LT-2) 3, a quartz discharge tube 4, evaporator 5, an apparatus for test samples 6, and vacuum taps K_1, K_2, K_3, and K_4. The discharge tube was a capillary 0.5 mm in diameter and 5-10 cm long. External electrodes were fitted on the wider end of the tube. The tube was connected to the vacuum system by means of two ground-glass joints.

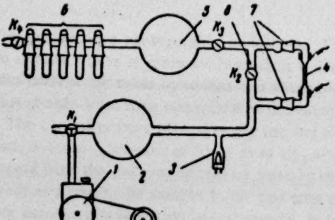

Fig. 1. Vacuum apparatus for evaporating test samples and obtaining discharges in water vapors.

Spectra were photographed on "Kodak 111-F" type plates; other plates can, however, be used which are sensitive to the red part of the spectrum. Photometric measurements were made on a non-registering microphotometer on the basis of a transformed blackening scale W.

2. Analytical Procedure

One of the brightest lines in the hydrogen spectrum Hα was chosen as the analytical line. The value of the isotopic displacement on this line allows one to use any diffraction spectrograph, or large prismatic spectrograph without using an interferometer. In Fig. 2 is shown a microphotogram of the lines H_α (6562.8 A) and D_α (6261.0 A) which demonstrates fairly good resolution.

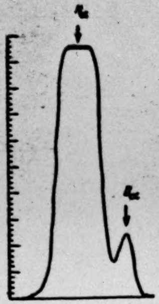

Fig. 2. Microphotogram of lines H_α and D_α.

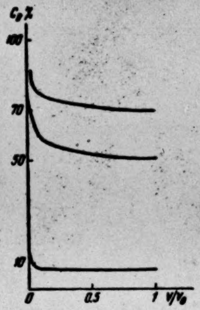

Fig. 3. Change in composition of test sample during evaporation.

Heavy and light water have somewhat different vapor pressures; accordingly the isotopic composition of the vapor differs from the composition of the liquid test samples with which it is in equilibrium. During evaporation, fractionation occurs and the test sample becomes richer in heavy water. In Fig. 3 are shown curves for fractional evaporation for a few samples of different concentration (9.51 and 72%). In this figure the ratio of the volume of test sample during evaporation to its original volume is plotted along the abscissa, while along the ordinate concentration of heavy water in the test sample is plotted. Since the difference in pressure of the saturated vapors of heavy and ordinary water changes with changes in temperature, then the isotopic composition of the vapors in equilibrium with the given test sample will also change with temperature changes. In order to avoid analytical errors connected with fractional evaporation, we decided to evaporate test samples completely and to analyze the isotopic composition of the vapors obtained. Under these conditions, the composition of the vapors corresponds exactly to the isotopic composition of the liquid test sample.

It was observed that the pressure in the discharge tube affects the value of the ratio of the intensities of H_α and D_α. In Fig. 4 is shown the curve relating I_D/I_H to pressure for a 50% concentration of D_2O in H_2O. From this diagram it is clear that this ratio decreases with decreasing pressure. Nevertheless, at low pressures, the discharge burns in a very unstable manner and the brightness of the glow decreases. Accordingly, for subsequent experiments, that pressure was chosen and used for carrying out analysis, at which the discharge was completely stable, and the brightness of the glow was a maximum. The generator operating conditions were also fixed so that the discharge had maximum brightness for the chosen vapor pressure in the tube.

Despite the fact that the discharge tube did not contain internal metallic electrodes, while the tube itself was made of quartz, evolution of hydrogen from the tube walls showed an essential effect on analytical results. Accordingly, the work was carried out in a stream of the vapors of the test material passing through the discharge tube.

The spectra were photographed as follows. The tubes for test samples (Fig. 1) were heated with a gas burner to remove traces of moisture from their walls. One drop of test sample (about 0.02 ml) was then introduced into each of the tubes by means of a clean pipet which had also been heat-treated to get rid of moisture. Tubes plus sample were then connected to the vacuum system via the ground-glass joint smeared with vacuum grease. The test tubes were placed in dry ice and air pumped out of the system and tubes through the ground-glass joint, down to a pressure of $5\cdot10^{-3}$ mm Hg, after which all the tubes with the exception of one were disconnected from the vacuum system by rotating the ground-glass joint. On closing taps K_2 and K_3, the dry ice is removed; as a result, the sample in the test tube connected to the system starts to evaporate into the evaporator. After complete evaporation of test sample, it is arranged, by means of K_1 and K_3, that a stream of vapor is passed through the discharge tube so that the vacuum gauge 3 registers 0.3 mm Hg; the high frequency discharge is then switched on and the spectra photographed through the three-stage attenuator. Spectra of samples with a concentration of 20-50% of one of the isotopes were photographed at an exposure of 5 sec; for concentrations 2-20%, the exposure time was 40 seconds. In the first case, both isotopic lines (H_α and D_α)

were photometrically measured without any attenuation of the spectra; in the second case the line of the isotope with the higher content in the mixture was photometrically measured at a transmittance of 29.0%, while the line of the other isotope was measured without attenuation.

3. Calibration Curve and Analytical Accuracy

The method of a constant calibration curve was chosen for carrying out analysis. In order to construct such a curve, special standards were prepared, uniformly spanning the concentration range 2 to 80% D_2O and H_2O. The standards were mixtures of ordinary distilled water and heavy water of known concentration. The mixed volumes were measured by means of a special micropipet shown in Fig. 5. Water was drawn up to the mark on the capillary. Pipets were calibrated by weighing. The error in measuring the volume of water with such a pipet was $3 \cdot 10^{-4}$ ml. It should be noted that in order to prepare a calibration curve it is essential to use freshly prepared standards, since on prolonged keeping, the composition of the standards changes appreciably. Table 1 contains results on the measurement of heavy water content of standards after storage in flasks with ground-glass stoppers in the course of two months. The spectra of freshly prepared standards were photographed three times on five photographic plates. Mean values of logarithm I_D/I_H were obtained for each standard from the results of photometric measurements. In Fig. 6 is shown a calibration curve which we constructed within the coordinates, logarithm I_D/I_H, logarithm C_D/C_H, expressing the relation between the ratio of line intensity and relative concentrations of the isotopes. The calibration curve is a straight line, which is slightly curved at lower concentrations. The angle made by the linear part of the graph on the concentration axis is slightly less than 45°. The curve is displaced to positive values of logarithm I_D/I_H with respect to the origin. This means that for a 50% test, the intensity of the deuterium line is greater than the intensity of the hydrogen line. All the characteristics noted here for the behavior of the calibration curve, for mixtures of D_2O and H_2O are completely confirmed by a relation established theoretically between the relative intensity of the isotopic lines and relative concentration of isotopes [3]. On this basis, it follows that the shift of the calibration curve is determined by differences in the physical properties of hydrogen and deuterium. The slope of the linear part of the curve is explained by the presence of some self-absorption in the lines H_α and D_α. The bend in the low concentration part is explained by superposition of the contour of the brightest line on the contour of the weak line, as is evident from Fig. 2.

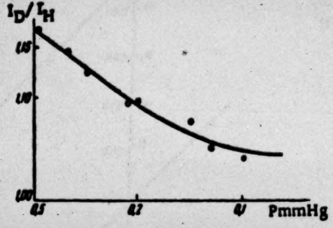

Fig. 4. Relation between ratio I_D/I_H and vapor pressure in the discharge tube.

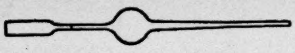

Fig. 5. Micropipet for exact measurement of small volumes.

TABLE 1

Date of analysis	Number of standard							
	1	2	3	4	5	6	7	8
July 12	80.83	70.9	49.74	27.67	17.89	10.22	4.51	2.48
Sept. 13	72.9	68.7	41.5	23.6	15.1	9.30	4.20	2.21

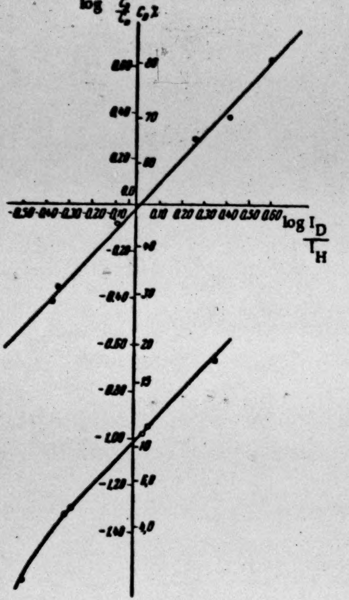

Fig. 6. Calibration curves for analyzing heavy water.

In order to determine the isotopic composition of a test sample by means of a microphotometer, the value of log $I_D/I_H = \frac{\Delta W}{\gamma}$ was determined. Corresponding values of logarithm c_D/c_H were obtained from the calibration curve, and from these concentrations were calculated by means of the formula

$$c_D = \frac{c_D/c_H}{1 + c_D/c_H} \quad 100\% .$$

So that it should be possible to determine the concentration of heavy water in the test sample at once, it is useful to give the concentration scale directly along the ordinate.

The accuracy of the method was established by analyzing some test samples of differing concentrations; the result of an analysis was taken as the mean of measurements of five spectra taken on one photographic plate. Table 2 contains the results of analyses of the percentage content of heavy water in several test samples, and the mean square error of one analysis. It is clear from the table that the relative error for low concentrations amounts to ~ ± 4% of the isotope with the lowest concentration; at high concentrations, the error drops to ~ ± 0.6 %. When one compares the method developed for isotopic spectrographic analysis of heavy water with the mass-spectrometric method [1], it is not difficult to conclude that the spectrographic method is no less sensitive than the mass-spectrometric method; on the other hand it has undoubted advantages with respect to speed and cheapness. In the case of spectrographic analysis, water vapor is studied directly, i.e., in the given case, the water is not converted into the gaseous phase by electrolysis as is necessary for determining the isotopic composition of water by the mass-spectrometric method. The great merit of the method developed is the independence of the results of spectrographic analysis of possible contamination of test samples, so that it is not necessary to carry out preliminary purification of the samples. It should also be noted that if operating conditions are more strictly controlled, and the spectra are registered photoelectrically, the accuracy of the method described can be increased considerably, as is evident from a paper published recently [6].

TABLE 2

Sample No.	Analysis No.									Mean	Mean square error	Relative error (%)
	1	2	3	4	5	6	7	8	9			
1	2.96	3.18	3.06	3.20	3.12	3.16	3.27	3,27	2.90	3.12	±0.13	4.2
2	11.42	11.96	11.69	11.79	12.1	11.75	12.0	12.0	11,8	11.8	±0.2	1.8
3	18.7	19.2	19.2	19.7	18.6	19.2	18.8	18.5		19.0	±0.4	2.1
4	48.2	48.8	48.5	48.0	48.2					48.3	±0.3	0.64

SUMMARY

A spectrographic method has been developed for the quantitative analysis of the isotopic composition of small volumes of heavy water. A calibration curve has been constructed which covers the concentration range 2-80% D_2O in H_2O. The relative error varies from ± 4 to ± 0.6%, depending on concentration.

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DETERMINATION OF LITHIUM IN ORES BY A FLAME SPECTROPHOTOMETRIC METHOD

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Determination of lithium in ores by chemical methods is long and laborious. Usually, the procedure used includes preliminary separation of the alkaline metals, followed by removal of lithium by extraction with organic solvents, and finally weighing as the sulfate. An analysis takes a few days, and the accuracy of the method is not high, particularly for low lithium contents.

Recently, flame photometry has found wide application for determining a number of elements, in particular the alkali and alkaline-earth elements; this method is based on direct photometric measurements of the light emitted by these elements in a flame [1]. Owing to the unusual simplicity of the technique, which reduces to a comparison of readings on a galvanometer for test samples and standard solutions, results can be obtained in a few minutes after getting the test sample into solution. The method has been used for determining lithium in ores [2-5], and in other objects containing silicates, glasses [6-7], and Portland cement [8]; nevertheless before carrying out the flame photometric part of the work in these analyses, the generally adopted, long and laborious methods of decomposing silicates were used, which involved treatment with hydrogen fluoride and sulfuric acids, or sintering by the Lawrence-Schmitt technique.

The problem we set for ourselves in the work described here was to assemble an apparatus from parts readily available, and to develop a rapid method of analyzing ores.

Apparatus. The flame spectrophotometer was assembled on the basis of the Ivanov scheme [9], using the UM-2 universal monochromator. In front of the inlet slit of the apparatus a burner made of molybdenum glass was set up on a support; the burner was connected to a glass, spherical, bulb-type T-piece through the side tube of which acetylene could be fed; the third tube, serving as an outlet from the bulb, was connected to the spraying chamber (Fig. 1). The sprayer was made from an ebonite cylinder, in the body of which were drilled 2 grooves of the same diameter (5 mm) as two glass tubes. The ends of the cylinder were slit and fitted with bolts whereby the separate parts could be tightened up and thus fix the glass tubes firmly in position (Fig. 2). The glass tube used for supplying air was drawn out so that the internal diameter at the outlet was 0.7 mm; the tube for bringing in liquid was drawn out to a diameter (internal) of 0.3 mm, and bent so that its end was opposite the outlet opening of the air tube. It can be reduced to size with a file. The tube was then fixed immovably by tightening up the bolt and screw; the other ends of the tubes are drawn out in opposite directions. A sprayer constructed in this way works quite well, and requires 4-5 ml of liquid per minute for an air pressure of 0.7-1 atmosphere. The sprayer was fed with air from a small compressor; acetylene for the burner was supplied from a cylinder fitted with a reducing valve and regulator; acetylene pressure in the apparatus after passing the regulator was determined by means of a water manometer and gave a reading of 10 cm water on connecting a capillary of cross section about 1 mm to the burner.

Measurement of the intensity of the 670.8mμ spectral line of lithium in the flame was carried out by means of an FEU-19 photomultiplier connected to a mirror galvanometer. The photomultiplier was placed in a box with an opening covered with glass opposite the photocathode. Inside the box was a voltage resistance divider (200 thousand ohms each) and a packet of silica gel for drying the air. The box was connected via its window to the outlet slit of the monochromator, from which it was separated by a protective glass disc and replaced by a UF-183 lens in a hood.

The photomultiplier was fed from dry batteries (12-16 BAS-G-80-L2.1 type batteries connected in series) or from a stabilized high-voltage rectifier, type VSE-2500 or something similar. Into the anode circuit of the photomultiplier was connected, via a voltage divider, a galvanometer type FI with a sensitivity of 400 mm/μa ($2.5 \cdot 10^{-9}$a/mm/M) and an oscillation period of 7 seconds. A ground-glass scale with millimeter divisions was fixed on a stand at a distance of 0.5 meter from the galvanometer, so that the galvanometer sensitivity was reduced to $5 \cdot 10^{-9}$a/mm. The galvanometer shunt allowed us to decrease the sensitivity of the galvanometer by factors of 2, 5, 10, 20, 50, 100 and 200. The electrical circuit is shown in Fig. 3.

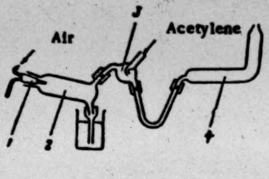

Fig. 1. Connections of sprayer and burner. (1) Sprayer, (2) sprayer chamber, (3) mixer, (4) burner.

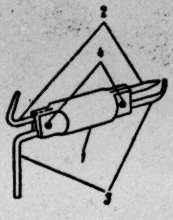

Fig. 2. Sprayer. (1) Ebonite cylinder, (2) tube for leading in air, (3) tube for leading in liquid to be sprayed, (4) bolts for tightening tubes.

Operational technique with the apparatus. After supplying air to the sprayer, the compressor is switched on, acetylene is fed to the burner which is then lit. The acetylene flow is regulated until a non-luminous flame is obtained. The burner is fixed in front of the inlet slit of the monochromator at a distance of 3-4 cm, so that the internal cone of the flame is 1-1.5 cm lower than the edge of the slit. The slits—inlet and outlet—are both 0.1 mm wide and 10 mm high. In order to isolate the spectral line of lithium, the monochromator drum is set according to the calibration curve at the division corresponding to the lithium line of 670.8 mμ. A solution of a lithium salt is introduced into the flame (about 50-100 γ/ml Li). On switching the photomultiplier on, the monochromator drum is rotated in both directions until maximum galvanometer reading is obtained. The position of the drum at which this is achieved corresponds to coincidence of the image of the lithium line with the outlet slit of the apparatus. The burner is then further adjusted by moving it slowly in front of the inlet slit until a maximum reading is again obtained. Actual measurements can then be made with the apparatus.

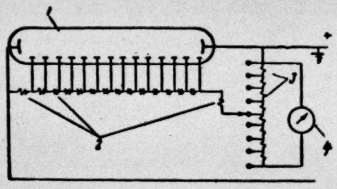

Fig. 3. Electrical scheme of the apparatus. (1) FEU-19 photomultiplier, (2) voltage resistance divider, (3) resistance shunt of the galvanometer, (4) galvanometer.

In order to get a reading, a small beaker (or crucible) containing test solution is brought up to the sucking end of the sprayer while the apparatus is operating, and then lifted up to the nozzle to allow solution to be sucked in. The galvanometer indicator swings when this is done and after about 10 seconds comes to a stop. Where two or more solutions are to be compared, readings are obtained successively for each of them, and then the whole series tested again in the reverse order and mean values taken. In this way it is possible to overcome the effect of small, gradual changes in air and acetylene pressures.

Sensitivity and specificity of lithium determination. In order to assess the suitability of the apparatus for work, the sensitivity and specificity of lithium determination was established. A lithium solution containing lithium in concentrations of 10 and 1γ/ml Li_2O (4.65 and 0.47 γ Li) was introduced into the flame and galvanometer readings taken. Sensitivity was expressed in terms of concentration of Li_2O in γ/ml corresponding to a galvanometer deflection of one scale division. The sensitivity of the FEU-19 photomultiplier depends to a considerable degree on the voltage [10]; consequently, measurements were made at different voltages. The results obtained are given in Table 1.

As can be seen from the table, a sensitivity of 0.01-0.02 γ/ml Li_2O can be achieved. For analysis of ores, however, a sensitivity of 0.4-0.1 γ/ml/ division and a voltage of 1300-1500 v are completely adequate.

We should like to note, in passing, that on using the ordinary city gas supply (using a Mekker burner but the same sprayer) the sensitivity obtained was 0.5-0.3 γ/ml at a voltage of 1800 v, i.e., the sensitivity is approximately 15-25 times less than with an acetylene burner.

In order to establish the specificity of the technique employed for lithium, galvanometer readings were taken for solutions of lithium salts at a definite voltage of the photomultiplier, and compared with readings obtained for solutions of other metals when the monochromator was adjusted for the lithium line. The existence of a photocurrent in the photomultiplier testified in this instance to insufficient monochromatization of the light and the presence of scattered light. As a standard of the suitability of the apparatus, a "specificity factor" was accepted; this is a number showing how much greater the reading obtained in the case of lithium is than that obtained in the case of another element when the concentration of lithium and the other element in solution is the same. Thus, the specificity factor

$$F = \frac{A_{Li} \cdot c_x}{c_{Li} \cdot A_x},$$

where A_{Li} and A_x are the readings obtained for solutions of lithium salts and another element, respectively, while c_{Li} and c_x are the respective concentrations.

In view of the nonlinearity of the relation between reading A and concentration c, the value obtained for F differs for differing concentrations; nevertheless, for chosen values of the concentration, F can be used for characterizing the suitability of the apparatus. The values obtained for F for the alkali and alkaline-earth elements are given in Table 2.

TABLE 1

Sensitivity of Lithium Determination at Different Voltages of the Photomultiplier

Voltage applied to photomultiplier in volts	1300	1300	1400	1500	1600	1700	1800	1900
Li_2O solution in γ/ml concentration	10	1	1	1	1	1	1	1
Reading	26	2.5	3.5	9	16	30	50	80
Sensitivity in γ/ml per scale division	0.39	0.40	0.29	0.11	0.06	0.03	0.02	0.012

TABLE 2

Specificity Factors for Determination of Lithium in the Presence of Alkali and Alkaline-Earth Elements (Slit 0.1 mm)

Element	Concentration of metal chloride in solution	Scale reading (in mm)	Specificity factor
Lithium	4.8 γ/ml	70	-
Sodium	1 mg/ml	18	840
Potassium	10 mg/ml	1	150,000
Cesium	10 mg/ml	5	30,000
Calcium	1 mg/ml	9	1,660
Strontium	1 mg/ml	250	60
Barium	10 mg/ml	13	11,500

As is evident from Table 2, high values of the specificity factor are obtained in the case of K, Cs, Ca and Ba (≥ 1000), they are somewhat less in the case of sodium, and very low in the case of strontium. The low value of the specificity factor in the case of strontium is explained by radiation in the 670 mμ region by a molecular band of the oxide SrO. As for sodium, the low value of F in this case can only be explained by the incidence of scattered light of wavelength 589 mμ from sodium on the photomultiplier. In the light of these results attempts were made to improve the apparatus by introducing supplementary light filters. Actually, it turned out that on introducing filters for absorbing the sodium radiation in the path of the light in the monochromator, in front of the output slit — didymium and light-red ruby glass — a considerably higher value of F was obtained, namely 77,000. Sensitivity of determination with didymium glass was not lower in these cases, but with the red filter sensitivity dropped 1.5 times. Thus, for flame photometric determination of lithium it is essential to use supplementary light filters.

After establishing the sensitivity and specificity of the method it was necessary to study the relation between intensity of the lithium radiation in the air-acetylene flame, and lithium concentration.

Sobolev, Mezhericher, and Rodin [11], have established that under similar conditions to those we used, the intensity of the lithium illumination is directly proportional to its concentration in the range 1-44 γ /ml. (Above this, the intensity of the illumination is proportional to $N^{0.42}$) We also got a linear relation between illumination intensity and concentration over the range 1-15γ /ml; moreover, this linearity was maintained over the range 0.1-1.0 γ /ml. Above 15 γ/ml of Li (about 30 γ/ml of Li_2O) the calibration curve bends toward the ordinate axis (Figs. 4 and 5).

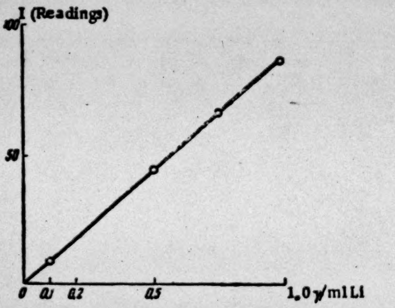

Fig. 4. Calibration curve for lithium concentrations of 0.1-1.0 γ /ml.

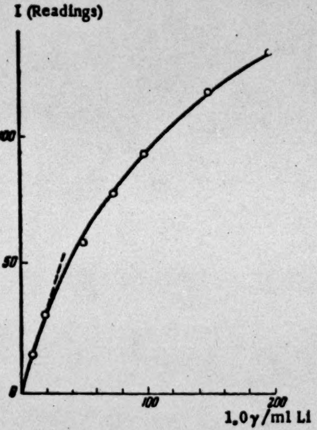

Fig. 5. Calibration curve for lithium concentrations of 10-200 γ /ml.

Determination of Lithium in Ores. For rapid decomposition of ores, and transfer of the lithium contained in them into solution, the method of fusion with potassium hydroxide was chosen; this has already been recommended for semi-microanalysis [12]. The analytical procedure is as follows. 0.5000 g of ore is fused with 3 g of potassium hydroxide in a silver dish, or in an iron crucible, over a gas flame or in an electric oven at 700° for 15 minutes. The melt, after cooling, is extracted with 50-60 ml water, and solution plus precipitate boiled in a beaker for 15 minutes while stirring with a mechanical stirrer. The solution is next cooled and transferred together with the precipitate to a 100 ml standard flask in which it is diluted to the mark with water. The solution is left to stand overnight and then filtered through a dry filter, the first portions being rejected, after which clear filtrate is measured flame photometrically by comparison with a series of standard solutions containing 0, 10, 25, 50, 75, 100, 125, 150, 175 and 200 γ/ ml Li_2O in a solution of 3% potassium hydroxide.

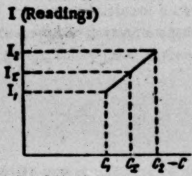

Fig. 6. Graphical calculation of lithium concentration C_x in the test sample from the readings of I_x for test solution and $I_{1,2}$ for the two standard solutions.

During these flame photometric measurements, readings are taken for test solution and two standards, one of which has a lower reading, and the other a higher reading then the one obtained with the test. Calculation of lithium content is made with the aid of a graph obtained by plotting lithium concentration in γ/ml along the abscissa and scale readings on the ordinate. Points corresponding to type solutions are plotted and joined by a straight line. At high lithium concentrations, the relation between J_λ and c is not linear; errors which can arise as a result of this however, can be minimized by choosing two standards whose concentrations are as close as possible to that of the test sample. Using this line, one can then get from the readings the concentration of Li_2O in γ/ml in the test solution (Fig. 6).

For converting the concentration of Li_2O in γ/ml to percentage of lithium in the original test sample, the following formula is used:

$$\%Li_2O \text{ in test sample} = \frac{a \cdot 100 \cdot 100}{1000 \cdot 500} = \frac{a}{50},$$

where a is the concentration found in terms of Li_2O γ/ml in solution.

We next considered the possible effect of other elements on accuracy of lithium determination. The solution obtained by fusing ores with alkali, may contain, in addition to the alkali metals which come from the ores, aluminum and silica, and also small amounts of alkaline-earth elements. The concentration of alkali metals which go into solution from the ore, is small in comparison with the concentration of potassium hydroxide used for fusion (30 mg/ml), and accordingly cannot show any appreciable effect. Aluminum and silica, as special tests showed, do not affect the intensity of the lithium illumination in potassium hydroxide solution, in concentrations of up to 2.5 mg/ml of Al_2O_3 and SiO_2 respectively (which correspond to a content of 50% of the oxides in the test sample). Of the alkaline-earth elements, the oxides or carbonates of which could dissolve in the alkali solution, only strontium could interfere; all the same, as tests showed, addition to a test sample of strontium salts in amounts corresponding to upwards of 20% SrO, did not change the readings for the test sample; apparently, because of precipitation of strontium as carbonate or hydrated oxides.

TABLE 3

Determination of Lithium in Rock Samples

Li_2O found chemically in %	Li_2O found photometrically in %	Deviation in %
0.07	0.07	0.00
0.13	0.11	-0.02
0.22	0.24	+0.02
0.60	0.54	-0.06
0.77	0.75	-0.02
1.01	1.03	+0.02
1.44	1.41	-0.03
1.53	1.59	+0.06
2.88	2.87	-0.01

Phosphates, added to samples of lithium ores (in amounts equivalent to upwards of 10% P_2O_5 in the sample) did not change, within the limits of experimental error, the amount of lithium found (samples contained about 0.8 and 4% of Li_2O). On addition to a solution of a lithium salt (10 and 100 γ/ml of Li) in 3% potassium hydroxide, of phosphates in amounts equivalent to 2.5 mg/ml P_2O_5, corresponding to 50% P_2O_5 (in test samples), the readings for lithium did not change when compared with readings for lithium solutions which were free of phosphates.

Nevertheless, during analysis of minerals containing much lithium and phosphates (amblygonites), it is possible to get low results, as a result of incomplete transfer of lithium into solution on extraction of the melt. In such cases, it is permissible to take a smaller amount of sample (0.2 g) or decomposition is effected with the aid of acids (hydrogen fluoride and sulfuric); after removal of excess acids, the residue is dissolved in water, 3 g of potassium hydroxide is added, the solution is boiled, and after dilution to 100 ml, analysis is carried out as usual.

A series of analyses of silicate rocks was carried out using the method developed; the analytical results obtained were compared with results obtained by chemical methods. As can be seen from Table 3, in which these results are given, fairly good agreement was achieved.

SUMMARY

The sensitivity and specificity of determination of lithium by a flame photometric method have been studied, using a spectrophotometer assembled from a monochromator, a photomultiplier, and a mirror galvanometer. The sensitivity of the method may be brought up to 0.012 γ/ml / division of Li_2O (1:83,000,000). High specificity of lithium determination in the presence of sodium can be achieved by using a supplementary light filter for absorbing the sodium radiation—a didymium glass or red glass. A rapid method of determining lithium in ores has been worked out; this is based on decomposition of the ores by fusing them with alkali and then carrying out flame photometric determinations on the solution obtained by leaching the melt. Using this method, it is possible to determine from 0.01 to 2-4% of lithium in ores in the course of 50 minutes with an accuracy of ± 2-4%.

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SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

PART II. DETERMINATION OF IMPURITIES IN THORIUM AND BERYLLIUM COMPOUNDS BY THE METHOD OF EVAPORATION IN A VACUUM*

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The basic principles and technique of spectrographic analysis by removal and concentration of the more volatile impurities from the less volatile main components, by fractional evaporation in a vacuum, with subsequent production of the spectra of the concentrate, have been considered in detail in a previous article [1]. In the present article we shall describe the application of this technique to determination of small amounts of impurities in thorium and beryllium compounds.

I. Spectrographic Analysis of Thorium

1. Conditions for Evaporation of Impurities

Of all the compounds of thorium, the most suitable for carrying out analysis by the evaporation method is the dioxide ThO_2, which is characterized by high stability and a high melting point (m.p. > 3000°); it is not hygroscopic, and can be readily obtained by calcining metallic thorium and a number of its compounds (nitrates, oxalates, etc.) in air. Its boiling point at atmospheric pressure is 4400° [2, 3]. Accordingly, it is possible to heat ThO_2 to a very high temperature in order to get rid of volatile oxides without any danger of evaporating the main component of the test. During evaporation under vacuum, a temperature of 1800-1900° proved sufficient for ensuring that almost all the elements to be determined were evaporated from test samples almost completely in the course of a minute. The exceptions were the oxides of beryllium and titanium which have a low volatility; for their determination it is necessary to carry out the evaporation at a higher temperature (2000-2100°).**

Figure 1 shows the completeness of evaporation of some impurities from ThO_2 samples under the chosen experimental conditions (50 mg of ThO_2 sample, temperature 1900°, duration of evaporation 60 seconds).

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* For Part I, see [1].

** Determination by the evaporation method of rare earths, calcium, zirconium, and some other elements, whose oxides are characterized by a very low volatility, is impossible or extremely difficult.

Completeness of evaporation of impurities, and repetition of the analytical results connected with this factor, depend to some extent on the weight of sample taken. *

Thorium dioxide does not undergo any change on heating under vacuum even up to very high temperatures; it differs in this respect from uranium dioxide which, as is known [4], changes over, on heating, into more volatile oxides; this process takes place very readily in the absence of sufficient atmospheric oxygen. As a result, the method of evaporating off impurities in a vacuum can only be applied with difficulty for spectrographic analysis of uranium dioxide.

2. Spectrographic Determination of the Impurities Separated

After we carried out the evaporation process, a thin and stable layer of condensed impurities was obtained on the front surface of the copper electrode, and this film was practically free of any of the main components of the test sample. Spectrographic analysis of the separated impurities was carried out by igniting the film in a condensed spark, using the following conditions for the oscillating circuit: L = 0.15 mH, C = 0.012 μF, and interelectrode distance d = 2 mm. The values used in the circuit, and the value of the spark gap, were selected as the result of a series of tests carried out to ensure maximum sensitivity for determination of most of the elements. Small deviations from the values given above have very little effect on the efficiency of the method. The spectra were photographed simultaneously on two or three spectrographs type K-24 (or ISP-22), KS-55, and ISP-51 with a camera whose focal length was 270 mm; choice of spectrograph depended on what element was to be determined. Exposure was chosen on the basis of the time the test elements took to burn out, and in the case of standard analyses amounted to 10 seconds.

TABLE 1

Analytical Lines and Sensitivity of Determination of Impurities in Thorium Dioxide

Test element	Analytical line	Sensitivity of determination in %	Observations
Li	6707.84	$1 \cdot 10^{-5}$	10 mg of sample can be used
Be	3130.42 3131.07	$1 \cdot 10^{-5}$	
B	2496.78	$1 \cdot 10^{-5}$	
Na	5895.93 5889.95	$1 \cdot 10^{-3}$	Increase in sensitivity limited by atmospheric contamination
K	7698.98 7664.91	$1 \cdot 10^{-3}$	
Mn	2576.10	$1 \cdot 10^{-5}$	
Cr	2835.54 2843.25	$1 \cdot 10^{-5}$	
Fe	2382.04	$2 \cdot 10^{-3}$	Increase in sensitivity limited by contamination of electrodes and graphite
Co	2378.68 2369.79	$5 \cdot 10^{-5}$	
Ni	2316.04 2394.51	$5 \cdot 10^{-4}$	
Cu	3247.54	$2 \cdot 10^{-4}$	Graphite electrodes used
Zn	2502.00 2557.96	$1 \cdot 10^{-3}$	

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* This question is treated in greater detail in Part IV which is included in the present issue p. 27.

In Table 1 are given the analytical lines used for test elements and the sensitivity of the determination. Spectrographic analysis was effected by the three standards method. The internal standard (gold) was only used for boron determination; but, as pointed out already [1], measurement of blackening of the control line (AU 2675 A) allowed one, with a high degree of confidence, to carry out spectrographic determination of the other contaminating elements by constructing a calibration curve in the coordinates ΔS, logarithm C (where ΔS is the difference in blackening of the analytical line and its immediate background).

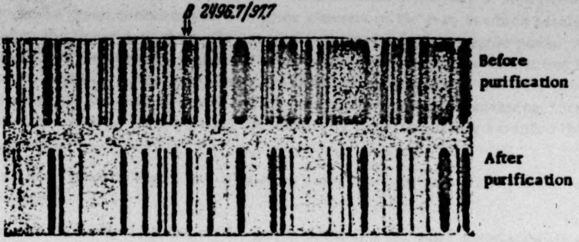

Fig. 1. Completeness of evaporation of some impurities from ThO_2 at 1900°.

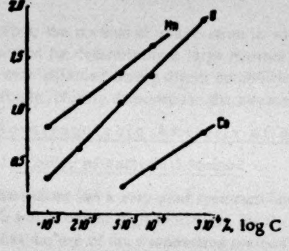

Fig. 2. Calibration curves for determining boron, manganese, and cobalt in ThO_2.

3. Standardization. In the determination of small concentrations of a large number of impurities, the question of standardization is an extremely vital one. The fact that the main component is not pure enough complicates the development of a method, and limits the possibility of increasing the sensitivity and accuracy of a determination. Chemical purificatication of thorium from traces of various impurities is fairly difficult [5]; accordingly, we decided to use as the main component for preparing standard mixtures, samples of thorium dioxide which had been given a preliminary treatment in the evaporation apparatus or in a high frequency vacuum oven. After evaporation of impurities in a graphite crucible there remains thorium dioxide which is spectrographically pure with respect to all volatile impurities to be determined (Fig. 1).

To thorium dioxide preliminarily purified in this way was added known volumes of standard solutions of the nitrates of the contaminating elements (boron was added as borax). From the primary standard prepared in this way (after calcining it in a crucible oven at 700°) the remaining standard mixtures were prepared by mixing it with various known amounts of the pure main component and grinding in an agate mortar.

The method just indicated for preparing the primary standard is simpler than the technique, also tried, which involves mixing solutions of the nitrates of thorium and the test elements and subsequent calcining to the oxides. Control tests showed that analytical results do not depend on which of the two methods was used for making the primary standard mixture.

In order that the composition of the standard mixtures approximates that of test samples, the test elements were introduced into the primary standard, not in equal amounts, but in amounts which were proportional to the content of the given element in type samples of ThO_2. This technique of preparing standard mixtures normally ensures a given analytical accuracy (the mean square error of a single determination is about 15% of the measured concentration). In certain cases, however, during analysis of nonstandard samples, there is considerable disagreement between composition of test samples and standards. In such cases an internal standard is used; an aqueous solution of $AuCl_3$ is added to the test samples and standards, respectively, immediately before evaporating the impurities.

We also used the method of additions [6,7] for accurate determination of the content of certain impurities in thorium dioxide samples, which were subsequently used as standards for spectrographic determination of impurities in other samples.

4. Analytical Results and Discussion of Results

The sensitivity of determination of individual contaminants (Table 1) is very high, and in many cases is greater than the sensitivity achieved by Scribner and Mullin [8], for analysis of the related element uranium, and also exceeds the sensitivity achieved by Cypres [5], who used the method of fractional distillation with a "carrier" for spectrographic determination of thorium. The concentration sensitivity of analysis was experimentally determined on the lowest given concentration of a given element in the test, at which blackening of the analytical lines is found on the linear part of the characteristic curve of the photographic plate. Such a rigid method of evaluating the sensitivity arose from general considerations concerning the connection between sensitivity and accuracy of the method. Actually, by using the three standards method, it is only possible to get the accuracy indicated above for the analysis (about 15%) in the region of normal blackening. Scribner and Mullin [8], who used less strict criteria for evaluating the sensitivity limit, arbitrarily extended the curve to intersect the abscissa ($\Delta S = 0$).

As an example, we have given in Fig. 2 the calibration curves used for determining boron, manganese, and cobalt in thorium dioxide.

The comparatively small scatter of points on the graphs illustrates the good reproducibility of the analytical results. Treatment of 55 spectrograms showed that the probable error for a single determination of boron in thorium dioxide by the given method amounts to 11.5%. Errors involved in determining other volatile elements in thorium dioxide are similar. Thus, the random error of the method is completely acceptable for spectrographic determination of such small concentrations. The use of an internal standard decreases the value of random errors by approximately one and a half times, and increases the reliability of the method considerably. The question of decreasing systematic experimental errors has been considered by us in a section devoted to standardization.

Thus, the method of evaporation in vacuum allowed us to develop a highly sensitive and reasonably accurate method for determining a large number of volatile impurities in thorium. The spectrograms shown in Fig. 3 which were obtained during direct combustion of ThO_2 samples in a D. C. arc and by the evaporation method respectively, clearly demonstrate the advantages of the new method.

II. Spectrographic Analysis of Beryllium

1. Choice of Analytical Method

Beryllium has a very poor spectrum and it would appear therefore that normal spectrographic methods of analysis would ensure high sensitivity for the determination of impurities in beryllium. Experiments showed however, that the use of the evaporation method in this instance led to a significant increase in the sensitivity of determination of several volatile impurities. It is particularly expedient to use this technique for solving the very important problem of determining boron. In this case, determination of boron is hindered by a group of fairly intense lines belonging to beryllium (2494, 56 A; 2494, 58 A; 2494, 73 A), which lie very close to the analytical duplet of boron (2496, 78 – 2497, 73 A). When the spectra are photographed during direct combustion, the boron lines are located on the wing of the overexposed group of beryllium lines, and only the use of a special spectrograph with very high dispersion can ensure reasonable sensitivity and accuracy of determination. Moreover, it is essential to bear in mind that determination of boron during combustion of test samples in a carbon arc is always complicated by the fact that this element is present as an impurity in graphite (and more so in carbon) electrodes. All these considerations led us to investigate the possibility of using the evaporation method for determining boron in beryllium.

Since boron oxides are considerably more volatile than beryllium oxide, then, in principle, it should be possible to select heating conditions for the BeO, such that the main component will be practically nonvolatile, while the boron oxide will evaporate from test samples almost completely. *Evaporation of boron oxide from BeO samples was carried out in vacuum.

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* Boron as an impurity in the graphite crucible from which evaporation is carried out does not lead to contamination of test samples, since the boron in graphite is combined as the carbide which does not evaporate at 2000°.

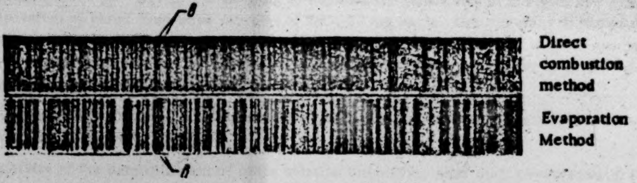

Fig. 3. Comparison of the evaporation method and the method of direct combustion for determination of boron in ThO_2. The spectrum of the same standard sample of ThO_2 containing 0.001% B_2O_3 was photographed in both cases.

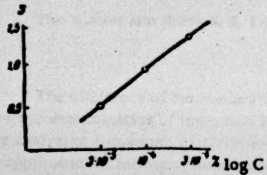

Fig. 4. Calibration curve for determining boron in beryllium.

BeO samples weighing 30 mg were placed in graphite crucibles and heated to 1750-1800°. Under such conditions, boron evaporated practically completely in 90 seconds, while beryllium oxide hardly evaporated at all.

The use of a large sample is complicated because of the low density of beryllium oxide. An internal standard ($AuCl_3$) was added to test samples and standards.

2. Spectrographic Determination of the Impurities Removed

Impurities removed by evaporation were burnt in a condensed arc under the conditions given above. It is desirable to use a spectrograph with a high dispersion (KS-55 or some other apparatus of the same class). since, under the conditions used for preparing the samples, small amounts of beryllium are deposited on the electrode. When a spectrograph of average dispersion is used, it should be remembered to take into account the uneven background created by the group of beryllium lines mentioned above. The spectrograms shown in Fig. 5, which were obtained on ISP-22 and KS-55 spectrographs, leave one in no doubt about the advisability of using a spectrograph with sufficiently high dispersion which ensures the possibility of carrying out determinations for a minimum background of the spectrogram.

We used the short-wave line composing the boron duplet as an analytical line (2496.78 A), since the more intense line of boron (2497.73 A) coincides with a strong line in the iron spectrum.

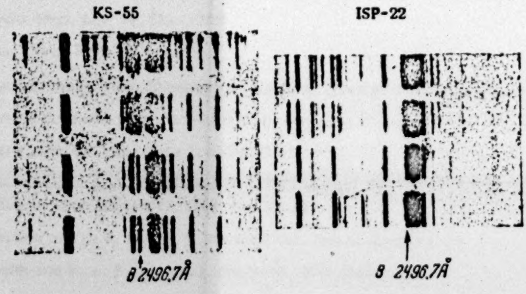

Fig. 5. Spectrograms of impurities removed during determination of boron in beryllium oxide, taken on spectrographs of medium and high dispersion (ISP-22 and KS-55).

3. Discussion of Results

The quantitative determination of boron in beryllium is readily carried out all the way up to concentrations of $3 \cdot 10^{-5}\%$ (Fig. 4). In order to increase the sensitivity of analysis, one can carry out successive evaporation of boron from three samples of BeO, 30 mg each. The accuracy of the method is characterized by the probable error for a single determination which is about 15%. The method can presumably be used for quantitative determination of elements whose oxides have the same order of volatility as that of boron oxide (Li, Na, Cd, Mn, etc.).

We have been unable to compare our method with others, since there is no published work on spectrographic determination of boron in beryllium.

The sensitivity of the determination of other volatile impurities, after their evaporation in vacuum, is not less than the sensitivity of the method involving distillation with a "carrier", as used by Smith and Fassel [9], for determining manganese and other elements in beryllium oxide.

During the development of the methods for analyzing beryllium and thorium, T. N. Ilinskaya, A. N. Razumovsky, V. P. Rotshtein, Z. N. Samsonova and P. P. Yakimova took part in solving some of the individual parts of the work. The authors wish to thank them.

The authors also thank S. E. Frisch for his constant interest in the work.

SUMMARY

The efficiency of the method of evaporation in a vacuum has been demonstrated, not only for spectrographic determination of impurities in compounds of elements which have a multilinear spectrum, but also for analyzing compounds of elements with poor spectra. It has been established that the evaporation method is applicable for solving various spectrographic analytical problems relating to the determination of a large group of volatile impurities in various high melting and low volatile compounds. In particular, apart from picked samples, the method is applicable for analysis of ZrO_2 and the oxides of some rare earths. Accordingly, one can speak of the universal applicability of this method.

The method is most effective for determination of traces of impurities in samples of a high degree of purity.

The presence of any impurities in concentrations of about 1% essentially decreases the sensitivity of determination of the remaining impurities, and makes it difficult to carry out the analysis in practice.

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QUANTITATIVE SPECTROGRAPHIC DETERMINATION OF BERYLLIUM IN ORES AND MINERALS

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Beryllium belongs to that number of elements which possess lines of high sensitivity, which appear in a carbon arc spectrum during evaporation of ores and minerals with concentrations of these elements greater than $n \cdot 10^{-5}$ %. As a result, semi-quantitative spectrographic analysis is widely used in the search for beryllium deposits, and for investigating the distribution of this element.

Quantitative determination of beryllium is a more difficult problem, and comparatively few papers have been published which have been devoted to accurate evaluation of this element in ores and minerals [1-3].

One of the fundamental difficulties which hinder quantitative evaluation of the beryllium content of ores is the relation between evaporation conditions of the element and the composition of the melt formed in the canal of the carbon electrode. Change in the composition of the test ore affects the passage of the elements into the arc flame, and destroys the character of the accumulation, and consequently depresses the concentration of the elements in the arc, and affects the kinetics of changes in line intensity during evaporation of test samples from the electrode canal [4, 5]. In addition, the change in composition of the test ore destroys the conditions of fractional evaporation of compounds of the elements from the melt; this leads to successive changes in the composition of the gas cloud in the arc, and consequently, in its temperature, which should be reflected in the intensity of the lines of the elements [6, 7]. Accordingly, for quantitative spectrographic determination of beryllium and other elements in ores, it is of great importance to establish conditions which will ensure increased reproducibility of evaporation of the elements, will decrease the effect of their fractional passage into the arc cloud, and will stabilize the temperature of the latter.

On the basis of our observations, these conditions are satisfied to a considerable extent by evaporating mixtures of the powdered ore with strontium sulfate and powdered carbon from the canals of a horizontal carbon A.C. arc [8].

In developing a technique for quantitative determination of beryllium in ores and minerals, using a horizontal arc for exciting the spectra, the problem was to determine 0.002-0.5% of beryllium with a probable error of ± 6 to 10%.

Determination of beryllium was based on photographing the spectra of the test ore, and measuring the difference in blackening of beryllium lines and elements used as internal standards added in constant amounts to the ore before its evaporation.

Calibration curves relating difference in blackening of the analytical pairs of lines to logarithm of beryllium concentration were constructed for each photographic plate on the basis of photometric measurements of standard powdered ores with a known content of beryllium.

In accordance with the requirements of technologists who are interested in enrichment of beryllium, attention was also devoted to developing a technique for rapid determination of small beryllium concentrations, which will ensure control of enrichment processes of beryllium ores and allow an analysis to be carried out in less than 25 minutes after reception of powdered sample in the spectrographic laboratory. In this case, determination of beryllium in ores was based on measurement of the relative intensity of the lines of beryllium and elements used as internal standards, by the method of visual interpolation [9]. Calculation of beryllium concentrations in ores was carried out by means of a three dimensional graph constructed within the parameters: logarithm of relative intensities of the lines and logarithms of the concentrations of beryllium in the ore, or by means of tables drawn up before hand. The accuracy achieved in this way was ± 10%.

1. Apparatus, Excitation Source, and Technique Used for Getting the Spectra

An A.C. arc struck between horizontally arranged carbon electrodes was used as the source of spectra excitation for analysis of beryllium ores and minerals.

The arc was supplied with a current of 15 amperes at a voltage of 220 volts.

Spectrographically pure carbon electrodes 6 mm in diameter supplied by the Kudinovsky factory "Electrougli" were used for making the electrodes. The electrodes were ground into the shape of cylinders 3 mm diameter and 10 mm long. Along the length of the cylinder a hole 8 mm deep and 1.5 mm in diameter was drilled. After filling the electrode canals with a mixture of ore and buffer powder, they were fixed (horizontally) in a stand at a distance of 4 mm; this distance was maintained constant during arc burning. Firing of the arc does not require the use of an activator and is realized by touching the tips of the electrodes.

During operation of the A.C. arc, a stable flame (directed upwards) is formed in which there is noted an even distribution of line intensities, the distribution being scarcely dependent on the properties of the elements; this permits one, when it is necessary, to select a zone in the flame with optimum conditions for the radiation of the lines of the elements [8]. An idea of the arrangement of the electrodes in the flame can be gained from Fig. 1. The part of the flame indicated in the diagram by the dashed circle was photographed; the light from this part was directed by means of a three lens illuminator on the slit of an ISP-22 quartz spectrograph. Satisfactory results were also obtained when the spectrograph slit was illuminated by means of a cylindrical lens with a focal length of 160 mm, which forms a vertical band of light on the spectrograph slit.

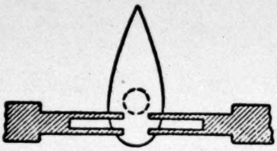

Fig. 1. Image of arc flame on the spectrograph slit.

"Spectrographic plates Type 1" with a sensitivity of 0.5 on the GOST scale were used for photographing the spectra. It should be pointed out that the duration for which the slit was illuminated (about 3 minutes) is determined by the time for complete evaporation of the powder placed in the electrode canal, since the arc goes out after the pointed ends of the electrodes have burnt off. An MF-2 microphotometer was used for measurement of the blackening of the lines on the photographic plates.

In this case, when a rapid determination of beryllium in ores by the method of visual photometry is required, the spectra are photographed with a ten stage quartz attenuator fitted on the spectrograph slit; this attenuator is supplied with the ISP-22 spectrograph.

2. Standard Ores Samples, "Buffer Mixture", and Preparation of Ores For Analysis

As preliminary tests showed, satisfactory conditions of stabilizing the arc flame temperature during passage of beryllium from test ores into the arc, could be achieved by adding to the ores large amounts of strontium which has a low ionization potential (5.7 electron volts).

On adding strontium sulfate to the ore, this element proceeds into the arc cloud at practically the same time as beryllium, aluminum, silicon, iron, calcium, and other elements which are found in the center of the volatility series of element oxides for a carbon arc [5, 10].

To the ore is also added feldspar which often accompanies beryllium; feldspar contains alkali metals with low ionization potentials (Na — 5.1 ev, K — 4.3 ev).

The requisite stabilization of evaporation conditions of the elements can be achieved by mixing test ores with a large amount of spectrographically pure carbon powder.

Therefore, in order to invalidate the effect of the composition of the test ore, and in order to create constant conditions for evaporation, as well as stabilizing the arc flame temperature, test ores were mixed in a proportion of 1 : 5 with "buffer mixture" consisting of 5 parts strontium sulfate, 2 parts of feldspar, and 5 parts of carbon powder.

The materials used for making buffer mixture should be tested first for absence of beryllium in them.

3.6% $BaCO_3$ and 11% V_2O_5 also enter into the composition of the buffer mixture, since both barium and vanadium are used as internal standards for determining beryllium.

After diluting test ores with buffer mixture, the powders obtained are placed, without weighing, in the canals of the carbon electrodes which are used subsequently for preparing the carbon arc.

Samples of ores which had been analyzed chemically, or samples of ore rich in beryllium, and subsequently diluted with a mixture of quartz and feldspar in the proportion of 1 : 3, were used for constructing calibration curves.

The base materials used for preparing standard samples of ores and buffer mixture were mixed by careful grinding in an agate mortar in the presence of alcohol.

3. Determination of Beryllium, In Ores

During determination of beryllium in ores by a method based on measurements of differences in line intensity, satisfactory results were obtained on using the analytical pair of lines Be I 2348.6 - Ba 2347.57 and Be I 2650.47 - Ba 2347.57, which embrace the beryllium concentration range of 0.002 to 0.5%.

Changes in ore composition over fairly wide limits did not lead to shifts in the calibration curves (Fig. 2) and consequently do not lead to development of systematic errors during beryllium determination.

The accuracy for beryllium determination, when two photographs of the spectra were taken, is characterized by a probable error of ± 6%. Results of spectrographic and chemical determinations of ores are given in Table 1.

Results of chemical analysis were obtained colorimetrically using quinalizarin.

For controlling enrichment processes of beryllium, in which analytical results on the enrichment of products poor in beryllium are required within 25-30 minutes after reception for analysis, the following analytical pairs of lines, which are sufficiently closely located, were used: Be I 2348.6 — Ba 2347.57 and Be I 2650.47 — V I 2654.0.

As can be seen from Table 2, the concentration range 0.002-0.04% is covered by the first pair, while the second pair covers the range 0.03-0.3%.

During photographing of the spectra through a multistage attenuator, and determination of the relative intensity of the analytical pairs of lines by the method of photometric interpolation, based on determinations of the equality of blackening of steps of the lines by examining the spectra under a spectroprojector, a linear relation was obtained between logarithm $\frac{I_{Be}}{I_{Ba,V}}$ and logarithm c.

The calibration curves for the analytical pairs of lines are given in Figs. 3 and 4.

In Table 3 are compared results for chemical and spectrographic analysis of beryllium ores.

The accuracy of a single determination of beryllium in ores is characterized by a probable error of ± 10%. It should be noted, however, that the relative intensity of the analytical pair of lines Be 2650.47–V 2654.0, in contrast to that of the pair of lines Be 2348.6–Ba 2347.57, depends on the composition of test samples, and can only be used for analyzing ores and their enriched products which are of sufficiently constant composition.

Actually, it is clear from Figs. 3 and 4 that changes over a wide range in the composition of test ores do not shift the calibration curves when working with the lines Be I 2348.6 and Ba 2347.57, but leads to a significant shift in the curves when they are constructed for the lines Be I 2650.47 and V I 2654.0.

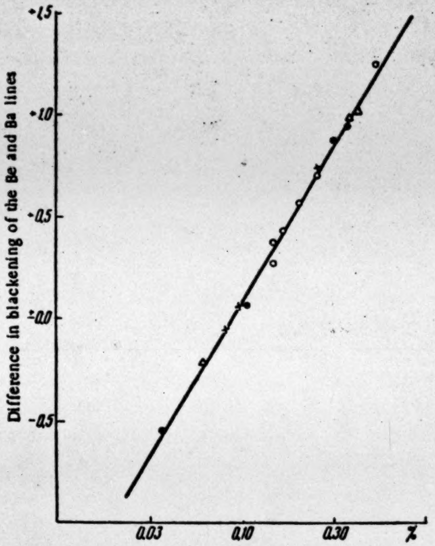

Fig. 2. Relation between differences in blackening of the lines Be 2650.47 and Ba 2347.57, and Be concentration in the ores. ●) Quartz-feldspar ore; ×) mica ore; Δ) fluorspar ore; o) iron ore.

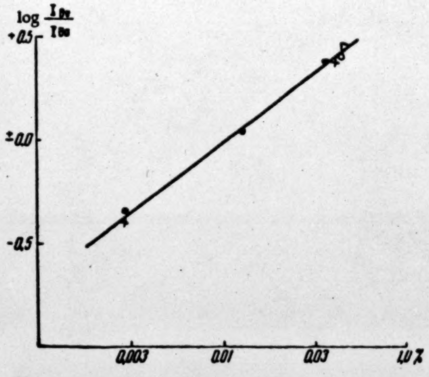

Fig. 3. Relation between differences in blackening of the lines Be 2348.6 and Ba 2347.57, and Be concentration in the ores. ●) Quartz-feldspar ore; ×) quartz-feldspar ore + quartz (1:3); Δ) quartz-feldspar ore + fluorspar (1:3); o) quartz-feldspar ore + mica (1:3).

TABLE 1

Results of Spectrographic and Chemical Analysis of Ores

BeO found in %		Relative experimental error in %	BeO found in %		Relative experimental error in %
spectrographic method	chemical method		spectrographic method	chemical method	
0.010	0.010	± 0	0.10	0.10	± 0
0.038	0.032	±18.7	0.15	0.16	— 6.3
0.042	0.038	±10.5	0.13	0.15	—13.3
0.062	0.065	— 4.6	0.18	0.17	+ 5.9
0.068	0.065	+ 4.6	0.29	0.27	+ 7.4
0.071	0.066	+ 7.6	0.43	0.41	+ 4.9
0.086	0.096	—10.4	0.54	0.54	± 0

TABLE 2

Analytical Lines

Analytical lines A	Internal standard content of buffer powder	Beryllium concentration range covered in %	Probable error in %	Time taken for an analysis	Method used
Be I 2650.47 Ba 2347.57	BaCO$_3$ 3%	0.03 —0.5	6.0	15 analyses in 8 hours	Measurement of line blackening on a microphotometer
Be I 2348.6 Ba 2347.57	BaCO$_3$ 3%	0.002—0.04	5.5	Ditto	Ditto
Be I 2650.47 V I 2654.0	V$_2$O$_5$ 9%	0.03 —0.3	10	One determination in 30 minutes	Measurement of relative intensities of the lines by the method of visual photometric measurements
Be I 2348.6 Ba 2347.57	BaCO$_3$ 3%	0.002—0.04	10	Ditto	Ditto

TABLE 3

Results of Spectrographic and Chemical Analysis of Ores by an Express Method

Be found in %		Relative experimental error in %	Be found in %		Relative experimental error in %
spectrographic method	chemical method		spectrographic method	chemical method	
0.012	0.010	+20	0.086	0.087	— 1.1
0.010	0.010	± 0	0.12	0.10	+20.0
0.016	0.017	— 5.9	0.10	0.11	— 9.1
0.017	0.018	— 5.5	0.21	0.20	+ 5.0
0.024	0.027	—11.1	0.24	0.23	+ 4.4
0.030	0.027	+11.1	0.13	0.15	—13.3
0.046	0.047	— 2.1	0.12	0.12	± 0
0.080	0.070	+14.2			

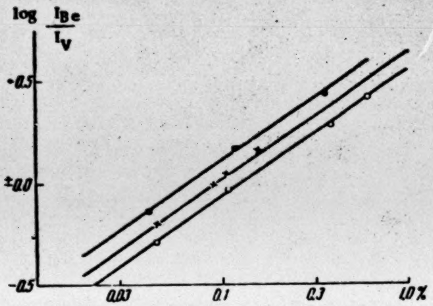

Fig. 4. Relation between relative intensity of the lines Be 2650.47 and V — 2654.0, and Be concentration of ore. ●) Quartz-feldspar ore; x) mica ore; o) iron ore.

It should be noted that the shift observed is mainly the result of a breakdown in the constancy of the background, and of changes in the general form of the spectra near the analytical lines, which lead, during visual photometric measurements of the lines, to erroneous evaluation of their relative intensity.

SUMMARY

1. A method has been developed for quantitative determination of 0.002-0.5% of beryllium in ores, with a probable experimental error of ± 5-6%, and an expenditure of 8 hours for carrying out 15 ore analyses.

2. An express method has been developed for quantitative determination of 0.002%-0.3% beryllium in ores and enriched products, which has a probable experimental error of ± 10%.

Two years experience in the use of the method in enriching factories has demonstrated the possibility of carrying out one analysis within 25-30 minutes of receiving the sample to be analyzed.

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[*] T.p. = C. B. Translation pagination.

SPECTROGRAPHIC ANALYSIS BY THE EVAPORATION METHOD

PART IV. DETERMINATION OF THE EXTENT OF CONDENSATION OF IMPURITIES*

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Spectrographic analysis by means of the evaporation method enables one to determine a number of readily volatile impurities in compounds of elements which are only slightly volatile with high sensitivity and reliability [1, 2]. Despite the wide application of this method, there is hardly any published information regarding the extent of condensation on the capsule (the condensing electrode) of the impurities being determined by evaporation from various materials. The relations between extent of condensation and geometrical factors, temperature, duration of evaporation, concentration of test elements and other elements, amount of test sample, etc., have not been studied sufficiently. Practical necessity dictates obtaining results on the extent of condensation; such results are of great interest for the application and further development of spectrographic analysis by the evaporation method.

EXPERIMENTAL

Radioactive indicators were used for determining the extent of condensation. The very slightly volatile oxides of beryllium, zirconium, lanthanum, thorium, uranium, and plutonium were used as test materials. The following radioactive isotopes, chosen for reasons of volatility and for convenience in work, were added to the compounds indicated.

Standards were prepared by three methods: 1) by precipitation: solutions of the nitrate or carbonates of test elements were added in corresponding amounts to a solution of the nitrate of the main element of a sample. After evaporation of the solution obtained, the precipitate was calcined at 500-600° for decomposition of nitrates or carbonates and preparation of oxides; 2) by moistening the oxide of the main element with a solution containing the nitrate or carbonate of test elements. After drying, the material was calcined to decompose nitrate and the final product ground in a mortar; 3) by mechanical mixing of appropriate amounts of the oxides. In all cases the radioactive indicator was introduced at the same time and in the same chemical form as the respective impurity.

The extent of condensation (condensation degree) is the ratio of the number of atoms condensed on the capsule to the number of atoms of the same element which was present in the test sample before evaporation [2].

The condensation degree K of any element was determined by comparing the activity of the condensate on a capsule with the activity of a radiometric standard (etalon)**, where the amount of radioactive material in this standard was taken as being equal to complete condensation of an impurity which evaporates completely from a test sample:

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* For Part III see Optics and Spectroscopy 2, No. 1 (1957).

** In the present article we mean by "etalon" a capsule (electrode) on the end of which there is placed a known amount of radioactive preparation. Under the term "standard" is to be understood a test sample containing a known amount of test elements, both radioactive and inactive.

$$K = \frac{I}{I_0} \qquad (1)$$

where I is the activity of the capsule plus condensate after evaporation; I_0 is the activity of the etalon.

The error in determining the condensation degree is made up of errors in measuring I and I_0. Determination of the value of I is accompanied by the following random elementary errors:

1) Error in weighing samples, m_1 (in %).

2) An error connected with inaccurate setting up of capsule with radioactive preparation at a definite distance from counter, m_2 (in %), calculated from geometrical considerations

$$m_2 = \frac{r^2\,dh}{(\sqrt{h^2+r^2}-h)(h^2+r^2)} \cdot 100\,\%, \qquad (2)$$

where h is the distance of the capsule from the counter filament; r is the radius of the counter window or diaphragm; dh the absolute error of setting the capsule at a definite distance from the counter.

3) The square error of counting the impulses, which is determined by the statistical nature of radioactive breakdown, m_3 (in %) [3, 4]

$$m_3 = \frac{\sqrt{\dfrac{I_{A+\Phi}}{t_{A+\Phi}} + \dfrac{I_{\Phi}}{t_{\Phi}}}}{I_{A+\Phi} - I_{\Phi}} \cdot 100\,\%, \qquad (3)$$

where $I_{A+\Phi}$ and I_{Φ} are the rates of counting impulses during measurements of the activity of a preparation ($I_{A+\Phi}$) and background (I_{Φ}), $t_{A+\Phi}$ and t_{Φ} are the times of measurement.

4) An error in preparing standards with a known content of radioactive impurity, m_4 (in %). Finally, the relative square error of measuring I is equal to

$$m_I = \sqrt{m_1^2 + m_2^2 + m_3^2 + m_4^2}. \qquad (4)$$

Measurement of I_0 is accompanied by random errors m_0, m_2, m_3, and accordingly, the error in determining I_0 will be given by

$$m_{I_0} = \sqrt{m_0^2 + m_2^2 + m_3^2}, \qquad (5)$$

where m_0 is the error in preparing a radiometric etalon.

The relative square error in determining the condensation degree is equal to

$$m_K = \frac{dK}{K} = m_I + m_{I_0}. \qquad (6)$$

In our case, the errors m_0, m_1, m_2, m_3, m_4 had the following values: $m_1 = \pm 0.4\%$; $m_2 = \pm 2\%$; $m_3 = \pm 2\%$; $m_4 = \pm 0.4\%$, $m_0 = \pm 0.4\%$.

Substituting these values in Formula (6), we find that the relative error in determining condensation degree is equal to ± 6%. At high temperatures (1800-2,000°), when evaporation and condensation of the main components, which have their own inherent radioactivity (plutonium, thorium, uranium), and which contained volatile fission products, commenced, corrections were applied to the results of measurements of the condensation degree; these corrections were determined in blank tests; error of measurement amounted in such cases to ± 8%. This order of accuracy is quite acceptable for spectrographic analysis by the evaporation method.

Relation between temperature and condensation degree is shown in Figs. 1 and 2, taking as examples the evaporation of zinc and bismuth. Ciphers 1, 2, and 3 attached to the curves indicate which of the three methods was used for preparing the standards. The temperature range covered by these tests was 800-2,000°. From Figs. 1 and 2 it is clear that the condensation degree at 1,600-2,000° is independent of the main component of a sample and of the method used for preparing the standards.

TABLE 1

Condensation Degree of Elements (Impurities) (in %) During Evaporation in Air (760 mm Hg) and Under Vacuum (10^{-2} mm Hg) at 1800°.* Duration of Evaporation 2.5 minutes; weight taken 50 mg; standard , 10^{-4} %.

Main element	BeO		ZrO_2		La_2O_3		ThO_2		U_3O_8	PuO_2	
	in air	under vacuum	in air	under vacuum	in air	under vacuum	in air	under vacuum	in air	in air	under vacuum
Bi^{210}	97	96	96	97	98	97	97	98	97	98	98
Sb^{122}	98	96	98	97	97	97	98	97	98	97	98
Cd^{115}	97	96	97	97	98	98	96	96	97	96	97
Na^{24}	87	95	83	94	85	95	87	96	86	86	95
K^{42}	86	95	85	96	86	95	85	96	87	86	95
Ba^{131}	5.5	5.5	5.6	5.5	5.5	5.6	5.5	5.5	5.4	5.3	5.5
Ni^{65}	53	63	51	60	50	61	54	62	51	52	63
Tl^{204}	97	97	97	97	98	98	97	98	98	97	97
Zn^{65}	96	97	97	97	96	98	97	98	96	97	97

Table 1 contains results on condensation degrees of test element-impurities for the most widely used evaporation temperature , 1800°. As can be seen from Table 1, the condensation degree, within the limits of experimental error, does not depend on the main component of a test sample.

The relation between condensation degree and amount of material taken is shown in Fig. 3, taking as an example evaporation of cadmium. A similar state of affairs is obtained during evaporation of the other elements. As can be seen from Fig. 3, condensation degree does not depend on sample weight, as long as the latter does not exceed 100 mg; at higher sample weights, condensation degree decreases with increasing amount of sample. Accordingly, in order to increase the sensitivity of small amounts of impurities, it is expedient not to increase the amount of sample, but to increase the number of capsules for obtaining one spectrogram. Evaporation of impurities from a large sample, apart from incomplete evaporation of the impurities from the latter, may lead to formation of a thick unstable layer of condensate on the capsule.

The relation between condensation degree and length of heating of the sample is illustrated on Fig. 4, taking evaporation of Na, K, and Ba from thorium oxide. During measurements, time was counted from the point where the given heating temperature was reached. The rate of heating was ≈ 30° per second.

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* By evaporation temperature we mean the temperature to which the outer surface of the internal beaker is heated [2].

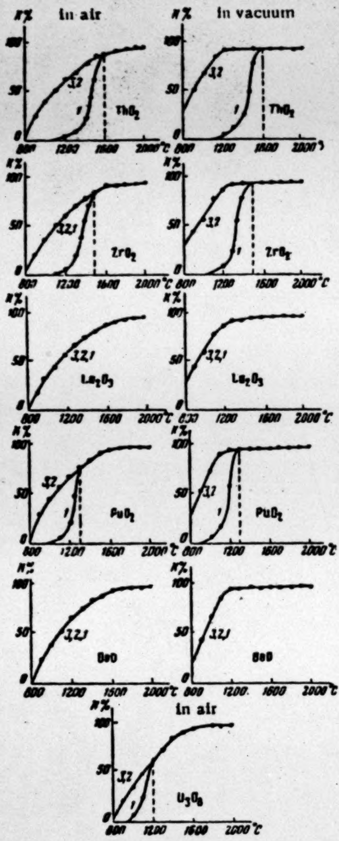

Fig. 1. Relation between condensation degree of zinc and evaporation temperature from different element oxides in air and under vacuum.

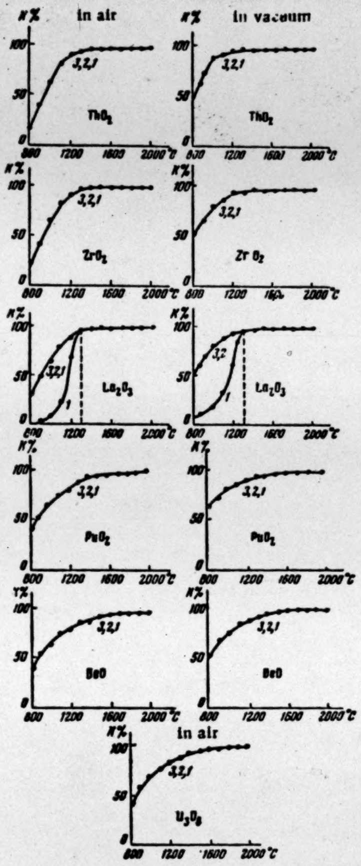

Fig. 2. Relation between condensation degree of bismuth and evaporation temperature from different element oxides in air and under vacuum.

From Fig. 4 it is clear that, starting at a certain point, further increase in duration of evaporation does not lead to any further increase in condensation degree. This point depends on the vapor pressure of test elements, and occurs earlier the higher the heating temperature and the smaller the amount of sample. During evaporation under vacuum, the time required for attaining the maximum value of the condensation degree is less than during atmospheric evaporation. In practice, for a sample weight of 50 mg, 2-2.5 minutes are enough for getting the maximum value of the condensation degree of all test elements (impurities).

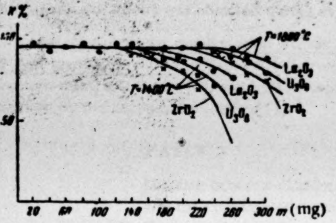

Fig. 3. Relation between condensation degree and amount of test sample for a cell of 4 mm diameter.

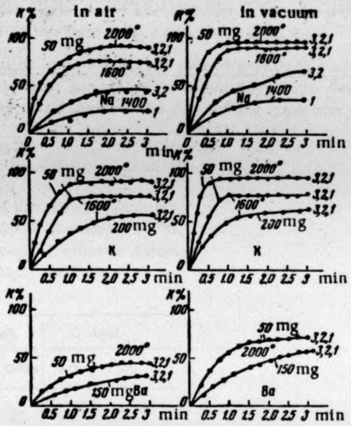

Fig. 4. Relation between condensation degree of test elements and duration of heating of the sample, in air and under vacuum.

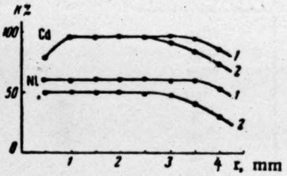

Fig. 5. Relation between condensation degree of elements and distance of capsule from vessel used for evaporation, for evaporation under vacuum 1, and under atmospheric pressure 2.

Test showed that if, after evaporation of the impurities at 1600-2000°, one removes the test sample from the evaporation cell, mixes it, stirs it, and then heats it up to the former temperature, then the condensation degree increases. By repeating this operation a few times, the condensation degree approximates 100%.

During evaporation of impurities below 1600°, the condensation degree increases only on stirring test samples prepared by the second and third methods, while for standards prepared by the first method, the condensation degree remains almost unchanged on stirring.

TABLE 2

Relation Between Condensation Degree of Elements (Impurities) and their Contents in Thorium Oxide; Evaporation Temperature 1800°; Duration of Evaporation 2.5 minutes; Sample Weight 50 mg (Vacuum)

Element	10^{-4} %	10^{-3} %	Element	10^{-4} %	10^{-3} %
Bi^{210}	98	97	Ba^{131}	5.5	5.6
Sb^{122}	96	96	Ni^{65}	61	62
Cd^{115}	98	97	Tl^{204}	98	96
Na^{24}	96	97	Zn^{65}	97	95
K^{42}	93	94			

Relation between condensation degree and concentration of test elements is illustrated in Table 2, taking evaporation of impurities from thorium oxide as an example.* As can be seen from the table, the condensation degree, within the limits of experimental error, does not depend on the concentration of the elements. A similar state of affairs was observed during evaporation of impurities from ZrO_2, La_2O_3, BeO, U_3O_8, PuO_2.

Relation between condensation degree and the presence of large amounts of other elements or carriers in test samples is shown in Table 3. Carriers were used by Scribner and Mullin for determining impurities in uranium using a D C arc [5], and by Mandelshtam, Semenova, and Turovtseva for determining impurities in uranium by the evaporation method [1].

TABLE 3

Relation between Condensation Degree of Elements (Impurities) and the Presence of Carriers in Test Samples. Standard 10^{-4}%, Temperature 1800°; Duration of Evaporation 2.5 minutes; Sample Weight 50 mg (Evaporation in Air from U_3O_8 and ThO_2)

Element	Without carrier		C Ga_2O_3		C AgCl	
	U_3O_8	ThO_2	U_3O_8	ThO_2	U_3O_8	ThO_2
Cd^{115}	98	97	97	98	98	97
Sb^{122}	98	97	97	96	98	97
Bi^{210}	98	98	98	98	97	97
Na^{24}	85	86	82	83	84	86
K^{42}	84	85	84	85	85	84
Ni^{65}	52	54	56	55	53	54
Ba^{131}	5.2	5.3	5.3	5.4	5.4	5.5
Zn^{65}	98	97	98	98	97	97
Tl^{204}	98	98	98	97	97	98
Ag^{110}	66	68	64	67	67	69

In order to study the effect of the carrier on condensation degree, gallium oxide or silver chloride in 2% amounts were added to test samples.

As can be seen from Table 3, the condensation degree, within the limits of experimental error, does not depend on the presence of carrier in the test.** Similar behavior was observed for evaporation of impurities from thorium oxide in a vacuum.

It should be noted that the condensation degree of Ag as an impurity does not depend on the presence of Ag as a carrier in a test sample. This seems to be added proof of the fact that the condensation degree is independent of concentration over a wide concentration range (10^{-4} - 2%).

Relation between condensation degree and distance of the capsule (point of condensation) and the vessel used for evaporation is shown in Fig. 5, taking evaporation of cadmium and nickel as an example. It is obvious that the condensation degree of impurities should decrease with increasing distance $\underline{r}$ between evaporation surface and condensation surface. On the other hand, at low values of $\underline{r}$, the condensation degree may also decrease as a result of possible secondary evaporation of condensate from the capsule heated by the hot vessel containing the sample to be evaporated. Consequently, at some definite point the condensation degree should have a maximum value.

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* The concentration range investigated was 10^{-4}-10^{-2} %.

** A more detailed discussion of carriers is contained in [6].

As can be seen from Fig. 5, the condensation degree of readily volatile cadmium initially increases with increasing r, attains a maximum value, and then starts to drop. The condensation degree of nickel, which is not readily volatile, is independent of r at low values of r, since the temperature to which the capsule is heated is insufficient for evaporating nickel.

It is also clear from Fig. 5 that the condensation degree, within the limits 1-2.5 mm, is independent of the distance of condensing surface from evaporating surface, both for cadmium and nickel. An appreciable drop in condensation degree starts at $r > 2.5$ mm for evaporation under atmospheric pressure, and at $r > 3.5$ mm in the case of evaporation under vacuum. There is no need to set the capsule very carefully at distances within the range 1-2.5 mm, since very small changes in r have hardly any effect on condensation degree.

DISCUSSION OF RESULTS

The experimental work which was carried out led us to the following conclusions:

1. In the temperature range 1600-2000°, the condensation degree of the elements, within the limits of experimental error, is independent of the main component of test sample (Table 1 and Figs. 1 and 2).

2. In the evaporation temperature range 800-1600°, condensation degree depends, to a minor extent, on the main component only when standards are prepared by the second and third methods (Figs. 1 and 2).

3. For the first method of preparing standards, the condensation degree of zinc during its evaporation from the oxides of plutonium, thorium, zirconium, and uranoso-uranic oxide; of antimony during its evaporation from the oxides of plutonium, thorium, zirconium, and lanthanum; of thallium during its evaporation from the oxides of thorium, and finally, of sodium during its evaporation from the oxides of thorium and lanthanum, depends essentially of the main element in the evaporation temperature range 800-1600° (Figs. 1 and 2).

4. During evaporation of impurities from beryllium oxide, the condensation degree of test elements is independent of the method of preparing standards in the evaporation temperature range 800-2000° (Figs. 1 and 2).

The close relation between condensation degree of the enumerated elements and the main element of the sample, and the method used for preparing the standards, when evaporation is carried out in the temperature range 800-1600°, leads one to assume that when standards are prepared by precipitation, those elements acting as impurities get into the crystalline lattice of the main component of the test.

In actual fact, the condensation degree of all elements, during evaporation from standards prepared by the second and third methods, is almost independent of the main component on heating in the range 800-1600°, since on introducing the elements serving as impurities into the main component by mechanical mixing or by moistening the main component with a solution containing the impurity elements, the latter, apparently, cannot get into the crystal lattice of the main component of the test. Curves 2 and 3 on Figs. 1 and 2, therefore coincide with each other completely.

On the other hand, during preparation of standards by the precipitation method, elements serving as impurities may get into the crystal lattice of the main component, and, in this case, the condensation degree of the elements which get into the crystal lattice will depend to a very large extent on the main component (Curve 1 on Figs. 1 and 2).

Thus, on the basis of experimental data on the relation between condensation degree and evaporation temperature, it may be considered that during preparation of standards by precipitation, the oxides of the following elements will penetrate into the crystal lattice of plutonium oxide (a cubic lattice of the fluorite type [7]): zinc, antimony, cadmium; while into the lattice of thorium oxide (cubic [8]), the following oxides will penetrate: those of zinc, cadmium, thallium, antimony, and sodium; into the lattice of zirconium oxide (cubic [8]): the oxides of zinc, antimony; into the lattice of uranoso-uranic oxide: zinc oxide; into the lattice of lanthanum oxide (hexagonal [8]): the oxides of cadmium, bismuth, antimony, thallium, and sodium.

Elements acting as impurities obviously do not penetrate into the lattice of beryllium oxide, since curves 1, 2 and 3 coincide completely with each other.

A comparison of the ionic radii of the impurity elements with those of the main components showed that the ionic radii of those elements which, according to results on the condensation degree, penetrate into the crystal lattice, are near in value to those of the main components.

The ionic radius of beryllium differs essentially from the ionic radii of test impurity elements.

Freeing of impurity elements from the lattice of the main component occurs at that temperature, above which curve 1 coincides completely with curves 2 and 3. This temperature at which the elements are freed from the crystal lattice is related directly to the melting point of the main component: the ratio of the absolute temperature at which impurities are released from the lattice of the main component, to the absolute melting point of the main component is approximately 0.55, and does not depend on the main component and evaporation conditions (under vacuum or at atmospheric pressure). Actually, the absolute melting point of thorium oxide is 3323° K (3050° C) [9]; the mean temperature at which complete release of impurity K from the lattice occurs, is, according to our results (see Fig. 1 and 2), approximately 1833° (1560° C). The ratio of $T_{release}/T_{melting}$ for thorium oxide is equal to 0.55.

For lanthanum oxide $T_{melting}$ = 2588° K (2315° C) [10]; the temperature of complete release of impurity from the crystal lattice is approximately 1593° K (1320° C); $T_{release}/T_{melting}$ for lanthanum oxide is approximately 0.61. For zirconium oxide, $T_{melting}$ = 2960° K (2687°C) [11, 12], $T_{release}$ is about 1723° K (1450°C); $T_{release}/T_{melting}$ is about 0.58. We were unable to calculate this ratio $T_{release}/T_{melting}$ for plutonium oxide and uranoso-uranic oxide because no information is available on the melting points of these oxides. The temperature of release of impurity elements from the lattice of plutonium oxide is, according to our results, about 1300°C,[*] while for the uranoso-uranic oxide lattice the temperature of release is about 1200°.

In order to check on the considerations just outlined, thallium was introduced into the lattice of calcium oxide (the ionic radii of thallium and calcium are very close to each other, 1.05 and 1.04 respectively). On Fig. 6 is shown the relation between condensation degree of thallium and temperature to which calcium oxide is heated (indices 1, 2, and 3 have their former significance). From this diagram it is clear that the temperature at which complete release of thallium from the calcium oxide lattice occurs, is approximately 1493° K (1220° C). The melting point of calcium oxide is 2858° K (2585° C) [13]. The ratio $T_{release}/T_{melting}$ is equal to 0.52.

Thus, at evaporation temperatures which are approximately 0.55 of the absolute melting point of the main component, there is, apparently, release of impurity elements from the crystal lattice of the main component, and the behavior of these elements above this evaporation temperature comes into line with the behavior of these same elements when they are not included in the lattice.[**] This release temperature proved to be near to the temperature of thermal disintegration of the crystal lattice.

In 1923-1928, Tamman, while studying chemical reactions occurring between powders, found that at temperatures approximately 0.57 of the absolute melting point, sintering of the salt powders and metal oxides occurs [14-17]. Tamman showed further, that during contact at a definite temperature of two powders which can react with each other, only a monomolecular layer of the reaction products is obtained and the reaction does not proceed further. On increasing the temperature, the amplitude of vibration of the atomic and ionic groups found in the nodes of the crystalline lattice, increases so much that these atomic and ionic groups start to pass through the monomolecular layer of reaction products and chemical interaction of the powders starts to proceed very intensively.[***] This temperature, on attaining which, there is an appreciable displacement of atomic and ionic groups, and a chemical reaction starts between powdered materials, Tamman called the temperature of initiation of internal diffusion [17]. According to his results, it is also about 0.57 of the absolute melting point, and coincides with the temperature at which powders start to sinter. Tamman showed further that at temperatures which are roughly equal to half the absolute melting point for metal salts and oxides, there should occur thermal disintegration of the lattices (Auflockerung), which favors an increase in the mobility of particles confined in the crystal lattice [18].

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[*] We are not considering here the application of the evaporation method to the analysis of other materials. The work in the case of plutonium oxide was carried out by A. I. Zaidel, N. I. Kaliteevsky, L. V. Lipis, and V. M. Tarakanov.

[**] Taking into account that the temperature of the test sample is in fact somewhat higher than the measured temperature of the wall of the vessel used for evaporation of test sample, the ratio indicated increases approximately to 0.60.

[***] Atomic and ionic groups in crystals are also displaced at temperatures corresponding to the transition point of one modification into another [17].

Presumably, the temperature of release of impurities from the lattice coincides with the temperature of disintegration, on reaching which, according to our results, volatile impurities leave the lattice. This temperature is about 0.60 of the absolute melting point of the main component and is practically invariable during evaporation under vacuum or in air at normal pressure.

This release of impurity elements from the lattices of the main components is most noticeable in the case of readily volatile elements (cadmium, antimony, bismuth, thallium, and zinc) which evaporate fairly intensively at disintegration temperatures.

A test sample is similar in structure to standards prepared by the first method. Accordingly, the temperature to which the sample should be heated during analysis must be higher than the disintegration temperature.

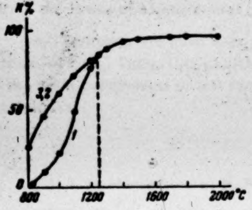

Fig. 6. Relation between condensation degree of thallium and temperature to which calcium oxide is heated.

Elements leaving the lattice of the main component diffuse through the mass of the sample. Increasing the evaporation surface, i.e., decreasing the length of the diffusion path, leads to an increase in the condensation degree. Agitation of sintered test samples which favors an increase in the number and size of the pores, through which vapor of impurities diffuse, also leads to an increase in condensation degree. Calcining a needle of sintered test material gives a similar effect.

Increasing evaporation surface and grinding test samples after evaporation, at temperatures lower than the disintegration temperature of the main component, do not lead to an increase in condensation degree.

Evaporating in a vacuum favors an increase in condensation degree. Apparently, when this is done egress of element impurities from the mass of test sample is facilitated into the vacuum after they leave the lattice of the main component.

As pointed out, the condensation degree of sodium, potassium, thallium, barium, zinc, cadmium, nickel, antimony, and bismuth, within the limits of experimental error, does not depend on the main component during evaporation at 1600-2000°. This fact is of great importance since it makes it possible, under certain conditions, to analyze certain elements using standards prepared on the basis of any one element.

From what has been said above, it is quite obvious that the operating temperature should be higher than the disintegration temperature of the sparingly volatile main component itself, since only in this case is the condensation degree, within the limits of experimental error, independent of the main component, or of the method used for introducing test elements into the standards. Nevertheless, the evaporation temperature should not be too high,either, otherwise evaporation and condensation of the most volatile main components on the capsule will occur, leading to interference with the spectra of impurity elements, and will affect the quality of the layer of condensate on the capsule.

It is clear that only when these conditions are fulfilled will it be possible to analyze any element by means of standards prepared on the basis of another. These conditions of analysis can be called conditions for mutual interchangeability of calibration curves.

It should be noted that for every concrete case of analysis, conditions under which curves can be interchanged must be checked experimentally. When there are only small deviations between curves, it is still possible to carry out an analysis by applying a correction factor.

SUMMARY

1. By using radioactive indicators, condensation degree has been determined for cadmium, antimony, bismuth, zinc, thallium, nickel, barium, sodium, and potassium during their evaporation from the oxides of plutonium, thorium, beryllium, zirconium, lanthanum, and uranoso-uranic oxide at 800-2000° in air (760 mm Hg) and under vacuum (10^{-2}mm Hg). The relative square error of determination amounts to ± 6%.

2. The relations between condensation degree and geometrical factors, temperature, duration of evaporation, sample weight, and concentrations of test and other elements, respectively, have been studied.

3. It has been shown that at 1600-2000°, condensation degree is independent of the main component, within the limits of experimental error.

4. Temperatures have been determined, on attaining which, impurities are liberated from the crystalline lattices of PuO_2, ThO_2, U_3O_8, La_2O_3, ZrO_2. These release temperatures are 0.60 of the absolute melting points of the main components of test sample, and are near in value to the temperatures of thermal disintegration of the lattices.

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* T.p. = C. B. Translation pagination.

STUDIES IN THE BEHAVIOR OF ULTRA SMALL AMOUNTS OF THE ELEMENTS

PART II. MECHANISM OF THE COPRECIPITATION OF RADIOISOTOPES WITH HYDROXIDES*

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It has been shown previously that the amount of radioisotopes coprecipitated does not depend on the molar solubility of $Fe(OH)_3$, $Th(OH)_4$, $La(OH)_3$, $Cd(OH)_2$, $Cu(OH)_2$, $Fe(OH)_3$ and other hydroxides, or on precipitation conditions [1]. There are two published opinions on the mechanism of coprecipitation. On the one hand, it is explained by mechanical trapping by the hydroxide precipitate of radiocolloids, formed by radioisotopes [2, 3]; and on the other by surface adsorption [4, 5]. An explanation of the real nature of coprecipitation of radioisotopes with hydroxides of various metals, apart from its theoretical significance, is very important for the practice of radiochemical analysis, since a knowledge of the processes which occur during such coprecipitation, will allow one to foresee the possibility of using it for removal of foreign elements from test solutions of radioisotopes.

Nevertheless, during a study of the nature of coprecipitation, one must bear in mind that formation of precipitates of various metal hydroxides is very complex and depends on many factors: concentrations of cations and OH ions, presence of foreign anions, the method used for precipitation, etc. During precipitation of hydroxides, basic salts are often formed, e.g., $10\,Al(OH)_3 \cdot Al_2(SO_4)_3$ [6], $Th(OH)_{3.31} \cdot (SO_4)_{0.35}$ [7], which lead to sudden changes in the ratio of the concentrations of cation and OH ions, at which formation of precipitate is observed [6], and which change the pH at which precipitation occurs [7], and the solubility of the precipitate.

All this makes it difficult to give a single interpretation of the results obtained.

Despite these facts, we have nevertheless made an attempt at studying the mechanism of coprecipitation of radioisotopes with hydroxides. To do this, a number of experiments were carried out on determinations of the extent of coprecipitation of the isotope Bi^{210} during formation of the hydroxides of iron, lanthanum, thorium, and cadmium, and of coprecipitation of Ce^{144} with iron and cadmium hydroxides. In these experiments 25 mg of the elements indicated above (10 and 100 mg, respectively, in the case of iron) were added in each case, and only partially precipitated as the hydroxides by gradual addition of a dilute solution of ammonia (1:20).

The relation found experimentally between the amounts of Bi^{210} and Ce^{144} respectively, coprecipitated, expressed as a percentage of the amount of the hydroxides of the metals indicated above, is shown in Figs. 1-6.

From the shape of these curves, it is clear that there is a linear relation between the amount of Bi^{210} and Ce^{144} coprecipitated and the amount of the hydroxides precipitated; the relative amount of coprecipitated radioisotope corresponds to the relative amount of hydroxide which separates out. Under these conditions, the change in the amount of metal in the range 10 to 100 mg, as is evident from Fig. 1, does not affect the relation indicated above. Some deviation is observed, but only on the initial part of the curves, when 20% of the hydroxide of the metal introduced is precipitated. For example, during coprecipitation of Ce^{144} with $Fe(OH)_3$, the amount of coprecipitated Ce^{144} is less than the amount of hydroxide which separates out, while the coprecipitated Bi^{210} is almost twice the amount of lanthanum hydroxide precipitated. A considerable deviation is observed during

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[*] A. A. Bragina and L. M. Saratov took part in the work.

coprecipitation of Bi^{210} with $Cd(OH)_2$. The curve obtained in this case shows that during precipitation of 40% of cadmium hydroxide, up to 80% of Bi^{210} is coprecipitated.

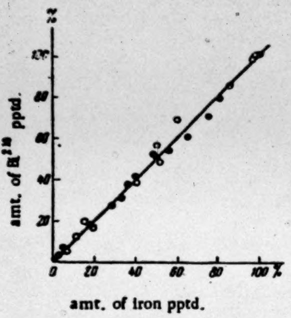

Fig. 1. Relation between amount of Bi^{210} coprecipitated and amount of ferric hydroxide which separates out (in %): ●) 100 mg iron; O) 10 mg iron.

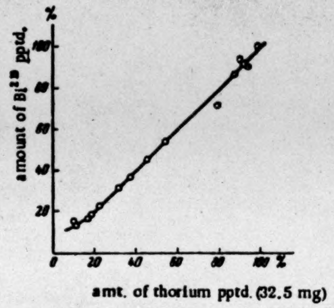

Fig. 2. Relation between amount of Bi^{210} coprecipitated and amount of thorium hydroxide which separates out (in %).

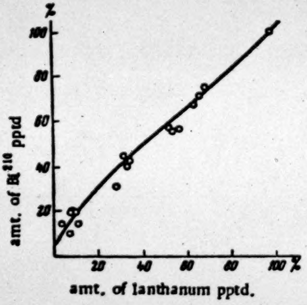

Fig. 3. Relation between amount of Bi^{210} coprecipitated and amount of lanthanum hydroxide which separates out (in %).

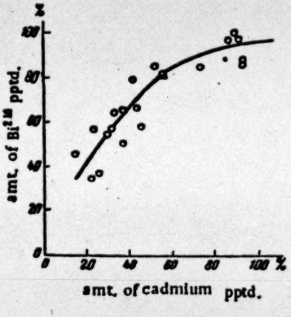

Fig. 4. Relation between amount of Bi^{210} coprecipitated and amount of cadmium hydroxide which separates out (in %).

In order to explain the results obtained, it is necessary to ascertain whether or not they depend on the pH at the commencement of precipitation of the hydroxides indicated above, and on their molar solubility. Though the latter values are not very exact, and depend, as was indicated above, on the conditions of formation of the hydroxide precipitate, they are nevertheless unique values, which, to a certain extent determine the properties of the hydroxides, e.g., the order of precipitation of the hydroxides of various elements [8-10], and their relative solubility. Accordingly, in order to find criteria by means of which it would be possible beforehand, even though only approximately, to determine the extent of coprecipitation of radioisotopes with hydroxides during their incomplete precipitation, we used pH values corresponding to the initiation of hydroxide precipitation from their dilute solutions [7], and the values of their molar solubility S [11], though strictly speaking, during incomplete precipitation, it is basic salts and not hydroxides which are precipitated.

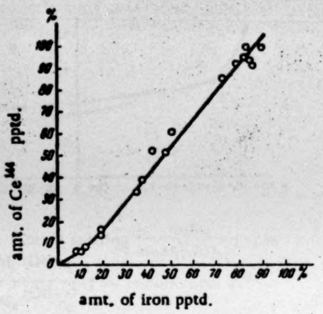

Fig. 5. Relation between amount of Ce^{144} coprecipitated and amount of ferric hydroxide which separates out (in %).

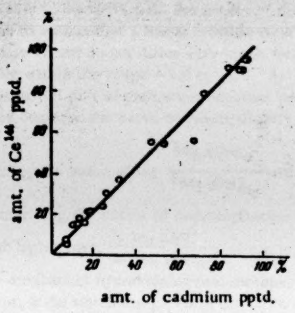

Fig. 6. Relation between amount of Ce^{144} coprecipitated and amount of cadmium hydroxide which separates out (in %).

TABLE

Hydroxides	Radio-isotopes	pH value for the initiation of hydroxide precipitation	S- molar solubility	$\frac{M_1(OH)_{n_1}}{M_2(OH)_{n_2}}$	$\log \frac{S_{M_1(OH)_{n_1}}}{S_{M_2(OH)_{n_2}}}$	$\frac{m_2 M_2^{n_2+}}{m_1 M_1(OH)_{n_1}}$
$Th(OH)_4$	Bi^{210}	3.5	$3.6 \cdot 10^{-10}$	$\frac{Th(OH)_4}{Bi(OH)_3}$	−1.48	$\frac{Bi^{210}}{Th(OH)_4}=1$
$Fe(OH)_3$	Bi^{210}	2(?)	$3.4 \cdot 10^{-10}$	$\frac{Fe(OH)_3}{Bi(OH)_3}$	−1.51	$\frac{Bi^{210}}{Fe(OH)_3}=1$
$La(OH)_3$	Bi^{210}	8.4	$9.2 \cdot 10^{-6}$	$\frac{La(OH)_3}{Bi(OH)_3}$	2.92	$\frac{Bi^{210}}{La(OH)_2}=1.25$
$Cd(OH)_2$	Bi^{210}	6.7	$3.9 \cdot 10^{-5}$	$\frac{Cd(OH)_2}{Bi(OH)_3}$	3.55	$\frac{Bi^{210}}{Cd(OH)_3}=2$
$Fe(OH)_3$	Ce^{144}	2(?)	$3.4 \cdot 10^{-10}$	$\frac{Fe(OH)_3}{Ce(OH)_3}$	− 2.1	$\frac{Ce^{144}}{Fe(OH)_3}=0.75$
$Cd(OH)_3$	Ce^{144}	6.7	$3.9 \cdot 10^{-5}$	$\frac{Cd(OH)_2}{Ce(OH)_3}$	1.0	$\frac{Ce^{144}}{Cd(OH)_3}=1$
$Bi(OH)_3$		4.5	$1.1 \cdot 10^{-8}$			
$Ce(OH)_3$		7.4	$4 . 10^{-6}$			

From the table which contains the results of these experiments, it is clear that coprecipitation of the radioisotopes Bi^{210} and Ce^{144} depend to only a minor extent on pH value at the initiation of hydroxide precipitation. For example, for Ce^{144}, the curves have almost identical shapes during precipitation with $Fe(OH)_3$ or $Cd(OH)_2$, although pH values differ very considerably among themselves (the difference between the pH values in these two cases is 5 units); for Bi^{210} on the other hand, there is observed a clear-cut difference in the nature of the curves for coprecipitation with $La(OH)_3$ and $Cd(OH)_2$, despite the fact that the pH values for beginning of precipitation in these cases are very close to each other.

On the other hand, the nature of the curves indicated above can, to a certain extent, explain the value of the ratio $\frac{S_{M_1(OH)n_1}}{S_{M_2(OH)n_2}}$, where $M_1^{n_1+}$ is the cation of the metal introduced, and $M_2^{n_2+}$ is the radioisotope cation.

A comparison of the value of the logarithms of the ratio adduced in the Table (column 5), with the nature of the curves, allows one to assume that a linear relation is only obtained when these values do not differ very much from each other, and lie within the range −1.5 to +1.5. As they increase, the initial part of the curves becomes convex, while as they decrease the curve becomes slightly concave.

By comparing the value of $\log \frac{S_{M_1(OH)_{n_1}}}{S_{M_2(OH)_{n_2}}}$ with the values characterizing the extent of coprecipitation of radioisotopes with hydroxides, $\frac{m_2\, M_2^{n_2+}}{m_1\, M_1\,(OH)_{n_1}}$ where m_1 and m_2 are the amounts of hydroxide or radioisotope which separate out, in %) which are given in the table (column 6) for the case where 20% of the metal introduced is precipitated, one could conclude that with increases in the first factor, coprecipitation of radioisotope with hydroxides will increase. This is clearly shown in the curve of Fig. 7, on which is depicted the relation between the values of $\frac{m_2\, M_2^{n_2+}}{m_1\, M_1\,(OH)_{n_1}}$ and $\log \frac{S_{M_1(OH)n}}{S_{M_2(OH)_{n_2}}}$ for the radioisotopes Bi^{210} and Ce^{144}.

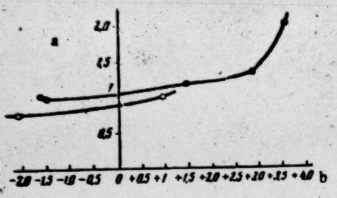

Fig. 7. Curves relating $\frac{m_2M_2}{m_1M_1(OH)_{n_1}}$ [a] to $\log\frac{S_{M_1(OH)_{n_1}}}{S_{M_2(OH)_{n_2}}}$ [b] for radioisotopes Bi^{210} and Ce^{144}; ●) Bi^{210}; ○) Ce^{144}

Consequently, it should be possible to estimate beforehand on the basis of the values of $\log \frac{S_{M_1(OH)_{n_1}}}{S_{M_2(OH)_{n_2}}}$, the extent of coprecipitation of the radioisotope $M_2^{n_2+}$ with a given hydroxide $M_1\,(OH)_{n_1}$ during its incomplete precipitation; e.g., for values of this factor ≥3, a large part (up to 80 %) of the radioisotope will separate out during precipitation as hydroxide of a small part of the nonisotopic carrier (20-40%). The latter fact is of great importance for the concentration of ultra-small amounts of elements, and the separation of radioisotopes in the presence of a large amount of foreign elements.

Let us now turn directly to the mechanism of coprecipitation of radioisotopes with the hydroxides of various metals.

All that has been said above testifies to the fact that coprecipitation of radioisotopes with the hydroxides of various metals cannot be explained either by adsorption coprecipitation (excess OH ions are necessary for this) nor by simple mechanical trapping by separation of deposits of the hydroxides of radiocolloids, which the radioisotopes of many elements form on adding NH_4OH.

One of the most probable mechanisms which explains the relation established between the extent of coprecipitation of radioisotopes and the amount of hydroxide precipitated, is the following. On addition to a solution containing a comparatively large amount of $M_1^{n_1+}$ cations and ultra-small amounts of the radioisotope $M_2^{n_2+}$, the first portions of the dilute ammonia form colloidal particles of hydroxide to which the following formula can be attributed [12], if one does not take into account formation of basic salts and ions of the type $[M_1\,(OH)]^{(n_1-1)+}$, $[M_1\,(OH)_2]^{(n_1-2)+}$, etc. For the metal hydroxide $[M_1\,(OH)_{n_1}]_{m_1}\cdot p_1\, M_1^{n_1+},\ n_1\,(m_1-x)\ A^{k-}]$; for the radioisotope hydroxide $[M_2\,(OH)_{n_2}]_{m_2}\cdot p_2 M_1^{n_1+},\ n_1(m_1-x)\ A^{k-}]$, where A^{k-} is the anion and m_1 and m_2 is the number of molecules of hydroxide in the nucleus of a colloidal particle; p is the number of adsorbed metal cations; $n_1(m_1-x)$ is the number of counter ions A^{k-} of the adsorbed layer. Such a structure for the radiocolloidal particle will mean that the radioisotope can lose its "individual" properties and will possess the properties of the metal introduced. This is explained by the fact that the chemical and physical properties of colloidal particles are determined by the ions which are in a given solution in excess and leads to stabilization of these particles. In the given case − these are the ions of the metal introduced.

Loss of "individual" properties of elements in a colloidal state is observed in many cases. E.g., if gelatin is added to a colloidal gold solution, the resulting solution acquires all the properties of the latter. Thus, gold ceases to coagulate on addition of sodium chloride, while on the other hand it is precipitated by tannin. If, instead of gelatin a hydrosol of stannic acid is added, the resultant solution will react with various reagents like the stannic acid sol. Colloidal solutions of metals (bismuth, copper, etc.) stabilized by titanium, acquire all the properties of titanic acid. Alimarin [13], has shown that the colloidal state of the compounds of niobium, tantalum, titanium, zirconium, and tungsten, leads to abnormal "solubility" of the precipitates and to abnormal reactions of these elements with various reagents when they are present simultaneously in solution. For example: for solutions of niobium and tantalum in the presence of titanium, formation of the follow-systems is postulated.

In acid media: the following predominate

1) $TiO_2 - [mMe_2O_5 \cdot nH_2O]TiO^{2+}, 2Cl^-$;
2) $Me_2O_5 - [mTiO_2 \cdot nH_2O]MeO_2, Cl^-$.

In alkaline media: the following predominate

1) $TiO_2 - [mM_2O_5 \cdot nH_2O]TiO_3^{2-}, 2K^+$;
2) $Me_2O_5 - [mTiO_2 \cdot nH_2O]MeO_3^-, K^+$.

This hypothesis has been confirmed experimentally by determining the charge of these sols.

The radiocolloidal state of radioisotopes and their properties have been studied in fair detail, on the one hand by Khan and coworkers [14], who consider that formation of radiocolloids is connected only with adsorption of ions of the radioelements on other particles suspended in solution; and on the other by Starik [15], Paneth and others, who have shown that radiocolloids consist of particles of sparingly soluble compounds of the radioisotopes, while adsorption phenomena play a secondary role in favoring formation of crystallization centers. The radiocolloidal state of radioisotopes appears to be a peculiar characteristic of the behavior of elements at ultra small concentrations.

Radiocolloids behave characteristically: they react very slowly with electrolyte ions, they do not hydrolyze or undergo ion exchange on ion-exchange resins, and they are adsorbed on various materials (paper, glass, etc).

That the Bi^{210} under our experimental conditions is in a radiocolloidal state is borne out e.g., by the results obtained during a study of the adsorption of Bi^{210} on the ion-exchange resin KU-2 from solutions with different pH (from 0.2 to 8). The procedure used was as follows. Through a column of this resin in the ammonium form (at pH 0.2, in the H form) packed in a column 10 mm in diameter and 70 mm long, was passed 5 ml of solution containing Bi^{210}, and of a carefully established pH; the latter was measured on an LP-5 pH meter with an accuracy of 0.1 pH units. Another 30 ml of the solution with the same pH was then passed through, and the activity of the eluents measured.

The relation between the amount of Bi^{210} in these solutions and pH is illustrated in Fig. 8; from the shape of this curve it follows that in the pH range 2-8, the radioisotope Bi^{210} is in a radiocolloidal state, while at lower pH values it is in an ionic form.

These results are in agreement with those obtained by a photographic method [16].

All that has been said confirms the existence in a solution to which has been added a small amount of ammonia, of colloidal particles of the composition indicated above. On addition of more ammonia, these particles react with adsorbed M^{n_1+} cations, as a result of which the nuclei of the colloidal particles of the hydroxides of both the metal introduced and of the radioisotope itself, lose their charges, and adhering together, are precipitated at the pH of the precipitation of the given metal hydroxide. According to such a mechanism, the extent of coprecipitation of radioisotopes with various metal hydroxides depends on the capacity of the given elements and radioisotopes to form colloidal particles at a solution pH lower than that necessary for precipitation of the hydroxide. Since the capacity of elements to form colloidal particles is connected basically with the solubility of the corresponding compounds, it becomes comprehensible why the relation which has been established between coprecipitation of radiosotopes with various metal hydroxides can be explained by the ratio of the values of their molar solubilities. If the values of the molar solubilities of the

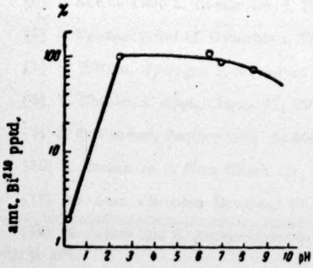

Fig. 8. Relation between Bi^{210} content of eluents and their pH.

metal hydroxides and radioisotopes differ very much from each other, then their capacity to form colloidal particles will be different. This also leads to deviation from a linear relation to one side or the other. On the basis of what has been said, it becomes clear why the nature of coprecipitation of radiosotopes with hydroxides depends to only a minor extent on the ratio of the pH values for the beginning of hydroxide precipitation, since these values are determined only by the beginning of coagulation of the colloidal particles already there.

Consequently, the mechanism described allows one to explain the character of the curves relating extent of coprecipitation of radioisotopes to amount of precipitated hydroxide. It should be noted, however, that this method does not exclude isomorphism or isodimorphism between the hydroxides of the radiosotope and the metal introduced, especially since x-ray structural, and other physicochemical studies, have shown a clearly defined crystalline structure for many hydroxides, e.g.: $Fe(OH)_3$, $Bi(OH)_3$, $Ce(OH)_4$, $Al(OH)_3$, $Mg(OH)_2$, etc. [16-17], although isomorphism may occur also in amorphous precipitates.

SUMMARY

The relation between extent of coprecipitation of radioisotopes and amount of precipitated hydroxide of a nonisotopic carrier has been studied. It has been established that the amount of radioisotope coprecipitated (in %) with the hydroxide is equal to the amount of hydroxide which separates out (in %). Deviations are only observed when a small amount of hydroxide (about 20%) is precipitated. The character of the relation indicated above allows one to postulate the following mechanism for coprecipitation with hydroxides; at pH values lower than that required for the beginning of precipitation of the hydroxide, formation of colloidal particles of the hydroxide of the nonisotopic carrier and the radioisotope with identical adsorbed cations occurs. During coagulation the nuclei of the colloidal particles of these hydroxides adhere together. According to this mechanism, it should be possible, from the logarithm of the ratio of the molar solubilities of the hydroxide of any metal and the radioisotope hydroxide, to estimate the extent of coprecipitation of the radioisotope with the given hydroxide during precipitation of the latter.

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EXTRACTION DURING RADIOMETRIC TITRATION

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Only precipitation reactions have been used for radiometric titration [1-6]. The radioactive indicator, which is contained in either the titrant or the solution to be titrated, is removed with the precipitate which settles out. In this way, either by the appearance or disappearance of radioactivity in the mother liquor, the end point can be established. It is obvious that the material being titrated together with the radioactive indicator can be removed from aqueous solution by another method also, e.g., by extracting the reaction product. Extraction could extend the field of application of such reactions. The work described here touched upon radiometric extraction titration. The following variants of radiometric titration with extraction of the reaction products can be envisaged.

1. The ion to be determined, labelled with its radioactive isotope, is titrated with a solution of nonradioactive reagent dissolved in water or organic solvent; the reaction product, on shaking, transfers to the organic solvent layer (for example, titration of the salts of zinc, mercury, lead and other elements with a solution of dithizone, or titration of zinc and mercury with hydroxyquinoline solution followed by extraction of the reaction product with chloroform, carbon tetrachloride, etc.).The shape of the titration curves are shown in Fig. 1,A.

As titration proceeds and the mixture is shaken, the activity of the aqueous layer decreases, while the activity of the organic solvent layer increases. These changes are only observed before the end point; after the end point the activity of the aqueous layer becomes practically zero, while the activity of the organic solvent layer becomes constant and equal to the original activity of the aqueous layer.

2. The ion to be determined is titrated with an aqueous solution of reagent, labelled with the corresponding radioactive isotope. The reaction product, in contrast to the reactant is soluble in organic solvents. For example, titration of potassium thiocyanate with a solution of cobalt sulfate marked with Co^{60} (water — isoamyl alcohol). The shape of the titration curve is shown in Fig. 1,B. In this case, the activity of the aqueous layer is practically zero up to the equivalence point; afterwards the activity of the aqueous layer increases. In the organic solvent layer the activity increases from zero up to the equivalence point, from here onwards it remains constant. The ascending parts of both curves are parallel to one another.

3. The ions to be determined, as well as reagent, are labelled with their isotopes. The reaction product, in contrast to the reactants, is soluble in the organic solvent. The suggested shape of the titration curves is shown in Fig. 1,C. Here the activity of the aqueous layer first drops to zero at the equivalence point and then increases. The activity of the organic solvent layer increases from zero to some constant value, which is higher than the initial activity of the aqueous layer. The ascending parts of both curves are not parallel to one another. If the labelled reagent can dissolve in the organic solvent layer, then titration is impossible.

Below is described a suggested method for titration of zinc and mercury with dithizone, with extraction of the dithizonates formed with chloroform (titration by the first variant).

Determination of Zinc

First we tried titration of zinc salts labelled with radioactive isotope Zn^{65}. The amount of indicator added corresponded to 10-50 γ zinc and was characterized by an activity of about 140 impulses / minute/γ zinc. The activity of the aqueous layer and of the chloroform layer respectively, during titration and extraction, changes as shown in Fig. 1,A. It can be understood that the progress of titration can be followed both on the basis of the activity of the aqueous and of the chloroform layers (or only on the basis of one of these layers). Determinations were carried out as follows. In test tubes fitted with ground glass stoppers were placed 1 ml lots of zinc salt solution containing Zn^{65} as indicator, and 1 ml lots of acetate buffer solution with a pH of 4.75. It is this pH which

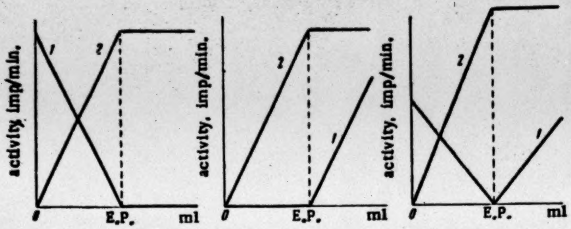

Fig. 1. Shape of curves obtained during radiometric titration with extraction of reaction product: A) radioactive ion-inactive reagent; B) inactive ion-radioactive reagent; C) radioactive ion-radioactive reagent
1) Aqueous layer; 2) organic solvent layer; E.P. Equivalence point.

is recommended for the photometric determination of zinc [7, 8]. According to other results [9], zinc dithizonate is also stable at pH 3.5-5. To the same test tubes were added various amounts of a dithizone solution in chloroform, and also pure chloroform in such amount that the volume of the chloroform layer in each test tube was 2 ml. The fact that both layers were equal in volume facilitated comparison of results obtained during studies of their activity. The contents of the test tubes were shaken on a mechanical shaker for 15 minutes. As tests showed, this period of time was fully sufficient for achieving equilibrium. The test tubes were centrifuged for 1-2 minutes to get fullest possible separation of the layers.

Table 1 contains the results obtained by this method for titration of 0.115 mg of zinc with dithizone solution.

TABLE 1

Radiometric Titration of Zinc with Dithizone Solution in Chloroform

Dithizone solution added in ml		0	0.25	0.5	1	1.25	1.5	2
Activity of 1 ml of liquid in impulses/minute	aqueous layer	2150	1565	940	0	0	0	0
	chloroform layer	5	620	1240	2115	2115	2070	2140

The curve showing the activity of the aqueous layer, as well as that showing the activity of the chloroform layer, exhibit a break at exactly the same point, in the given case at 0.86 ml of dithizone solution. The titer strength of the dithizone solution with respect to zinc is equal to 0.115/0.86 = 0.133 mg/ml.

It must be noted that the titer of the dithizone solution, according to our observations, changes very little in the course of a long time (more than a month), in agreement with published results [8]. Thus, extraction which is applicable to radiometric titration is also convenient in that it is possible to measure simultaneously, both the activity of the aqueous layer and that of organic solvent layer, and, consequently, simultaneously carry out two determinations in parallel. Total activity of the aqueous and chloroform layers should be, within the limits of experimental errors, equal at all points. The initial activity of the aqueous solution should be equal to the final activity of the chloroform layer. The latter is only true for indicators with a fairly large radiation energy. In the opposite case, the electrolytes in solution (buffer solutions) can absorb part of the radiation. Nevertheless, as will become evident later, this fact does not affect the position of the end point. Zinc content was determined by the method described above. In order to establish the equivalence point graphically, it is necessary to know the activity before beginning titration, and during the course of titration (2-3 points), and also after passing the equivalence point (2-3 points). By means of such results, a curve like that shown in Fig. 1,A is constructed. It is possible to measure the activity of both the aqueous and chloroform layers. It is simple to determine the volume of titrant solution necessary for reacting with the amount of cation taken; the method does not require measurement of activity after the equivalence point. In this case it is necessary to distinguish between determinations on the basis of activity of the aqueous layer, from determinations according to the activity of the chloroform layer. Calculation, on the basis of the two points during studies of the activity of the aqueous layer, is carried out by means of the formula:

$$V_x = V_1 \frac{A_0}{A_0 - A_1}, \qquad (1)$$

where V_x is the volume of the dithizone solution in chloroform used for titration which is required for attaining the equivalence point, in ml; V_1 is the volume of the chloroform titrant added, in ml; A_0 is the activity of a known volume of the aqueous solution before beginning titration in impulses/minute; A_1 is activity of the same volume of aqueous layer after addition of V_1 (in ml) of titrant and extraction, in impulses/minute.

TABLE 2

Radiometric Determination of Zinc (the Percentage error is given in Parentheses)

Zinc content of sample in mg			Zinc found in mg			
amount taken	amount of indicator added	total	aqueous layer		chloroform layer	
			total	total	total	initial amount
0.285	0.015	0.30	0.31 (3,3)	0.295 (3,5)	0.31 (3,3)	0.295 (3,5)
0.194	0.056	0.25	0.22 (12)	0.164 (15)	0.22 (12)	0.164 (15)
0.112	0.048	0.16	0.18 (12,5)	0.132 (18)	0.17 (6,2)	0.122 (8,9)
0.086	0.048	0.136	0.14 (3)	0.092 (7)	0.14 (3)	0.092 (7)
0.077	0.048	0.125	0.12 (4)	0.072 (6,5)	0.12 (4)	0.072 (6,5)
0.067	0.048	0.115	0.12 (4)	0.072 (7,5)	0.12 (4)	0.072 (7,5)
0.059	0.048	0.107	0.11 (3)	0.062 (5)	0.09 (16)	0.042 (29)
0.048	0.01	0.058	0.059 (2)	0.049 (2)	0.059 (2)	0.049 (2)
0.041	0.01	0.051	0.047 (8)	0.037 (7)	0.046 (10)	0.036 (12)
0.029	0.01	0.039	0.039 (0)	0.029 (0)	0.039 (0)	0.029 (0)
0.019	0.01	0.029	0.030 (3,5)	0.020 (5)	0.031 (7)	0.021 (10)

In principle, formula (1) does not differ from the formulas for calculations during radiometric titration by the precipitation method [2,5]. During analysis of the chloroform layer, calculation by means of two points is only possible for work with an indicator with a large radiation energy, or for work with aqueous solutions containing small amounts of dissolved salts which are not capable of appreciably absorbing the radiation of the indicator. When these conditions are observed, the radioactivity of the organic layer at the equivalence point is equal to the initial activity of the aqueous layer, so that calculation can be made by means of the formula:

$$V_x = V_1 \frac{A_0}{A_1},$$

where V_x, V_1, and A_0 have the same significance as in formula (1); A_1 is the activity of the chloroform layer after addition of V_1 (in ml) of titrant and extraction, in impulses/minute.

TABLE 3

Determination of Zinc by Radiometric Titration on the Basis of the Activity of the Aqueous Layer [calculated by means of formula (1)]

Zinc taken in mg	Titer of dithizone solution in terms of zinc in mg/ml	Amount of titrant added in ml, V_1	Activity of 1 ml of aqueous layer in impulses/minute		V_x in ml	Zinc found in mg	Error in %
			A_0	A_1			
0.30	0.215	1.25	885	140	1.476	0.317	5.7
0.248	0.133	1.5	2970	340	1.69	0.224	9.7
0.21	0.133	0.25	3750	3150	1.57	0.208	1.0
0.163	0.133	0.5	2105	1310	1.32	0.175	7.4
0.152	0.133	0.25	2960	2330	1.17	0.155	2.0
0.134	0.133	0.5	2220	1090	0.982	0.131	2.2
0.125	0.133	0.5	2270	1015	0.90	0.12	4.0
0.115	0.133	0.5	2152	940	0.88	0.117	1.7
0.106	0.133	0.5	2215	875	0.83	0.110	3.8
0.096	0.133	0.5	3600	1415	0.828	0.110	14.6
0.086	0.133	0.5	2210	430	0.62	0.082	4.6
0.064	0.133	0.5	3370	140	0.522	0.069	7.8
0.058	0.029	1.25	800	300	2.0	0,058	—
0.051	0.029	1.25	760	170	1.61	0.047	8
0.046	0.029	1.0	820	230	1.4	0.041	11
0.039	0.029	1.0	744	200	1.37	0.040	2.6
0.029	0.029	0.25	790	575	0.92	0.027	6.7

TABLE 4

Determination of Zinc by Radiometric Titration on the Basis of the Activity of the Chloroform Layer [calculated by means of formula (2)]

Zinc taken in mg	Titer of dithizone solution in terms of zinc in mg/ml	Amount of titrant added in ml, V_1	Activity of 1 ml of $CHCl_3$ layer in impulses/minute		V_x in ml	Zinc found in mg	Error in %
			A_0	A_1			
0.30	0.215	1	990	660	1.5	0.32	6.6
0.248	0.133	1.5	3000	2360	1.9	0.25	0.8
0.21	0.133	0.25	3700	525	1.76	0.23	10
0.163	0.133	0.5	2080	815	1.27	0.169	3.7
0.152	0.133	0.25	3100	665	1.16	0.154	1.3
0.134	0.133	0.5	2270	1108	1.02	0.136	1.5
0.115	0.133	0.25	2140	620	0.86	0.114	0.9
0.106	0.133	0.25	2140	710	0.75	0.10	5.7
0.086	0.133	0.25	2180	850	0.64	0.085	1.2
0.064	0.133	0.25	3400	1680	0.5	0.066	3.1
0.058	0.029	0.5	790	200	1.97	0.057	1.7
0.054	0.029	1.25	800	635	1.6	0.046	10
0.039	0.029	1.0	750	590	1.27	0.037	5
0.029	0.029	0.25	820	210	0.98	0.028	3.5
0.022	0.029	0.25	780	240	0.8	0.023	4.5

When working with softer radiation, as we have already observed, the maximum activity (A_0) of the aqueous layer is on the low side because of some absorption of the radiation by electrolytes.

Table 2 contains results for zinc determination in 1 ml of solution by the method indicated above, when the equivalence point is found graphically.

We see that the experimental results are completely satisfactory. It is understood that more accurate results could be obtained by adding practically weightless amounts of a radioactive indicator; we could not do this, however, because we did not have a zinc preparation with a high specific activity.

Table 3 contains the results of determinations obtained by calculating the equivalence points on the basis of the activity of the aqueous layer, while Table 4 contains results obtained on the basis of the activity of the chloroform layer.

Determination of Mercury

An analogous method was used for determining small amounts of mercury. In contrast to zinc, the reaction between mercury salts and dithizone is quantitative even in strongly acid media [7]. Accordingly, we used an acetate buffer with a pH of 0.65, 1 ml of which was added to 1 ml of test solution. The remaining conditions were the same as those used for zinc determination. It should be noted, however, that in contrast to zinc dithizonate, the equilibrium between the aqueous and chloroform layers in the case of mercury dithizonate is reached in 1-2 minutes. The radioactive mercury isotope Hg^{203} was introduced with the mercury in an amount of 0.01-0.02 mg; it had a registered activity of about 1500 impulses/minute. As a consequence of the low radiation energy, the initial activity of the aqueous layer was considerably less than the final activity of the chloroform layer. All the same, this circumstance is not reflected in the position of the equivalence point. As an example we have given in Table 5 the results of titrating 0.176 mg of mercury.

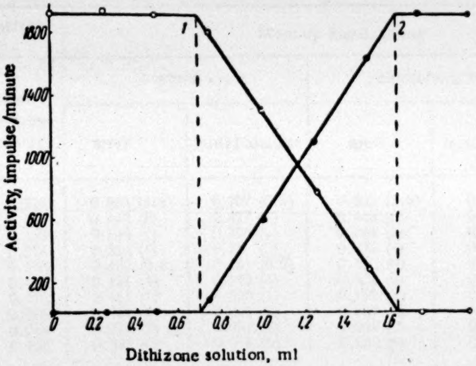

Fig. 2. Titration of mercury and zinc (indicator Zn^{65}): 1) activity of aqueous layer; 2) activity of chloroform layer.

Determination of mercury in solution by such a method gives satisfactory results whether one follows the activity of the aqueous layer or the chloroform layer (Tables 6-8).

Our experiments showed that a 100 fold excess of zinc has practically no effect on radiometric titration of mercury. The nature of the titration curves is similar to that of curves obtained in the absence of zinc. The latter is only true in the case of strongly acid media (pH 0.65). At pH >4, not only mercury dithizonate is formed and extracted but also zinc dithizonate. Nevertheless, mercury salts are titrated first, and then zinc salts. Consequently, by using the radioactive isotope Zn^{65}, it is possible to determine mercury and zinc when they are both present simultaneously in solution. In Fig. 2 are shown titration curves for 0.080 mg of zinc and 0.1 mg of mercury in 2 ml of buffered solution (pH 4.7).

As we have already pointed out, mercury is titrated first, the activities of the chloroform and aqueous layers respectively, do not change during this process. When all the mercury has been titrated, zinc starts to react with dithizone. The activity of the chloroform layer thereupon starts to increase while that of the water layer starts to drop. After the equivalence point, as usual, the activities of both layers become constant. It follows from Fig. 2, that 0.7 ml of dithizone solution was used for titrating mercury and 1.64-0.7 = 0.94 ml of dithizone solution for titrating zinc.

TABLE 5

Radiometric Titration of Mercury with Dithizone Solution plus Chloroform

Dithizone solution added in ml		0	0.25	0.5	0.75	1	1,25	1,5
Activity of 1 ml of liquid in impulses/minute	aqueous layer	950	600	325	0	0	0	0
	chloroform layer	0	400	900	1350	1360	1300	1350

TABLE 6

Radiometric Titration of Mercury (0.016 mg of mercury labelled with Hg^{203} added as indicator; equivalence point calculated graphically)

Mercury content in mg/ml		Mercury found, in mg			
		aqueous layer		chloroform layer	
Taken	Total (with indicator)	total	initial amount	total	initial amount
0.80	0.816	0.803 (1.6)	0.797 (0.4)	0.803 (1,6)	0.797 (0.4)
0.40	0.416	0.443 (6)	0.427 (7)	0.443 (6)	0.427 (7)
0.32	0.336	0.344 (2)	0.328 (2)	0.344 (2)	0.328 (2)
0.20	0.216	0.224 (4)	0.21 (5)	0.224 (4)	0.21 (5)
0.150	0.166	0.167 (0,6)	0.151 (0.7)	0.166 (0)	0.15 (0)
0.120	0.136	0.131 (4)	0.115 (4)	0.131 (4)	0.115 (4)
0.096	0.112	0.111 (1)	0.095 (1)	0.111 (1)	0.095 (1)
0.040	0.056	0.057 (2)	0.041 (2)	0.057 (2)	0.041 (2)
0.032	0.048	0.047 (2)	0.031 (3)	0.047 (2,	0.031 (3)
0.016	0.032	0.032 (0)	0.016 (0)	0.032 (0)	0.016 (0)

Thus, it has been demonstrated that it is possible to use a nonisotopic indicator (zinc) for determining mercury. Not only zinc, but other radioactive elements (e.g., cobalt) whose dithizonates have a higher instability constant than the corresponding compound of mercury, can be used as nonisotopic indicators. It is possible that Zn^{65} may also be a convenient nonisotopic indicator for titration of copper salts with dithizone.

TABLE 7

Radiometric Titration of Mercury. Determinations based on Activity of Aqueous Layer [equivalence point calculated by means of formula (1)]

Mercury taken in mg/ml	Titer of dithizone in terms of mercury in mg/ml	Amount of titrant added in ml, V_1	Activity of 1 ml of aqueous layer in impulses/minute		V_x in ml	Mercury found in mg	Error in %
			A_0	A_1			
0.416	0.275	0,5	575	400	1.65	0.454	9.1
0.336	0.275	0.75	575	230	1.25	0.343	2.0
0.216	0.22	0.5	225	110	1	0.22	1.8
0.176	0.22	0.5	950	350	0.79	0.174	1.1
0.136	0.234	0.25	575	315	0.55	0.129	5.1
0.112	0.275	0.25	450	160	0.43	0.118	5.3
0.056	0.047	0.75	425	175	1.28	0.06	7
0.048	0.047	0.5	475	275	1.2	0.056	16.6
0.032	0.047	0.5	325	140	0.85	0.04	25

TABLE 8

Determination of Mercury by Radiometric Titration on the Basis of the Activity of the Chloroform Layer (indicator Hg^{203}) [equivalence point calculated by means of formula (2)]

Mercury taken in mg/ml	Titer of dithizone in terms of mercury in mg/ml	Amount of titrant added in ml, V_1	Activity of 1 ml of chloroform layer in impulses/minute		V_x in ml	Mercury found in mg	Error in %
			A_0	A_1			
0.416	0.275	0.5	725	225	1.6	0.44	5.7
0.336	0.275	0.75	775	490	1.2	0.33	1.8
0.216	0.22	0.5	270	180	0.75	0.165	23
0.176	0.22	0.25	1350	380	0.9	0.198	12.5
0.166	0.22	0.5	925	630	0.73	0.161	3
0.136	0.234	0.25	625	275	0.55	0.130	4.4
0.112	0.275	0.25	775	425	0.45	0.124	10
0.056	0.047	0.75	760	475	1.2	0.056	0
0.048	0.047	0.5	660	325	1.0	0.047	2
0.032	0.047	0.5	525	375	0.7	0.033	3

SUMMARY

A method is described for radiometric extraction titration of micro amounts of zinc and mercury with a solution of dithizone in chloroform. It has been demonstrated that it is possible to use nonisotopic indicators for radiometric titration with extraction.

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THE APPLICATION OF β-HYDROXYNAPHTHOIC ALDEHYDE IN ANALYTICAL CHEMISTRY

3. GRAVIMETRIC SEMI-MICRO DETERMINATION OF BERYLLIUM

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In previous articles [1-3], it has been shown that β-hydroxynaphthoic aldehyde can be used for quantitative determination of magnesium and copper.

In the present article, the gravimetric semi-micro determination of beryllium by means of this reagent is discussed.

Preparation of the Beryllium Complex of β-Hydroxy-α-Naphthoic Aldehyde

To 200 ml of a solution of beryllium sulfate or chloride, containing about 0.05 mole of salt, was added 200 ml of a 2% alcohol solution of β-hydroxy-α-naphthoic aldehyde. The liquid was heated to 70°, and then, with constant stirring, a 10% ammonia solution added until precipitate started to separate out. The greenish-yellow crystalline precipitate was washed a few times with 50% alcohol and dried at 110°.

On the basis of the suggested formula $C_{22}H_{14}O_4Be$ it was calculated that Be is 2.57%, C 75.2% and H 4.02%. On the basis of the analytical results, the formation of the compound can be represented as follows:

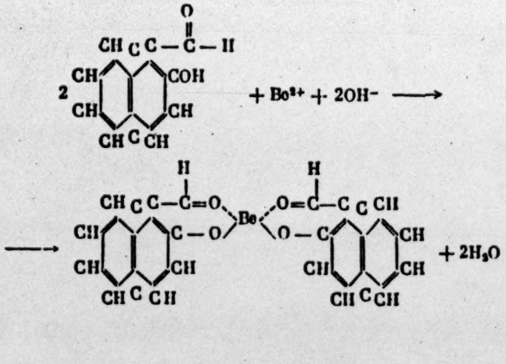


TABLE 1

Analysis of the Beryllium Compound

Weight taken in g	Obtained in g	Found in %
0.2500	0.0178 BeO	Be 2.40
0.1354	0.3740 CO_2	C 75.33
0.1354	0.0478 H_2O	H 3.90

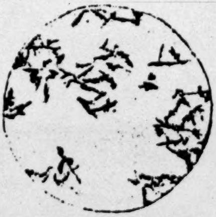
Some of the properties of this beryllium compound are given in Table 2.

Gravimetric Determination of Beryllium by Means of β-Hydroxy-α-naphthoic Aldehyde

To a solution of the chloride or sulfate of beryllium containing 1 mg/ml of Be, was added a 2% alcohol solution of β-hydroxy-α-naphthoic aldehyde (approximately about 5 times the theoretical amount). The liquid, after addition of the aldehyde, should contain not less than 50% alcohol, i.e., for each ml of solution was added 5 ml of 2% alcoholic solution of reagent and 4 ml of water. The mixture obtained was heated to the boil, and then gradually, with continuous stirring, 1 N ammonia was added until the solution smelled of ammonia. The characteristic greenish-yellow crystalline precipitate separated out immediately; it was filtered after 25-30 minutes through a No. 2 or No. 3 glass filter, it was then washed with 50% alcohol and dried at 110°. The conversion factor to beryllium is 0.02565.

TABLE 2

Properties of the Compound of Beryllium with β-Hydroxy-a-Naphthoic Aldehyde.

Color of crystals	Yellowish-green
Solubility in water at 15°	0.008%
in alcohol	0.038%
in 50% alcohol	0.05%
in ether	0.05%
Behavior towards 2N H_2SO_4	On heating the dry material with 2N H_2SO_4, the compound breaks down with formation of a clear solution; on cooling, the aldehyde separates out (It dissolves in alcohol)
Behavior towards concentrated HCl	Dissolved
Behavior towards 2N NaOH	Dissolves on prolonged boiling
Behavior on heating in a capillary in air	Does not melt, chars at 253°
Crystals form (magnification 120x)	

The results contained in Table 3 show that the gravimetric method of determining beryllium with β-hydroxy-a-naphthoic aldehyde in pure salts gives satisfactory results; experimental errors are not in excess of permissible limits.

In the presence of copper, iron, and aluminum salts, the disodium salt of ethylenediaminetetracetic acid (Complexone III, Trilon B) was used as masking agent. According to published results, beryllium in the presence of Complexone III, is quantitatively precipitated by ammonia as the hydroxide in the presence of Ca, Mg, Al, Fe, Cu, Cd, Zn and other cations.

TABLE 3

Determination of Beryllium in Pure Salts

Beryllium taken in mg	Weight of precipitate	Beryllium found in mg	Absolute error in mg
2.00	0.0760	1.95	−0.05
2.00	0.0770	1.98	−0.02
2.50	0.0964	2.47	−0.03
3.00	0.1136	2.91	−0.09
3.00	0.1196	3.07	+0.07
3.50	0.1392	3.57	+0.07
4.00	0.1594	4.09	+0.09
4.50	0.1774	4.55	+0.05

TABLE 4

Determination of Beryllium in Presence of Other Elements

Amount of beryllium in mg	Weight of the precipitate of the beryllium complex of ß-hydroxynaphthoic aldehyde	Beryllium found in mg	Absolute error in mg
3.00	0.1150	2.95	−0.05
3.80	0.1498	3.84	+0.04
3.80	0.1478	3.79	−0.01
3.80	0.1508	3.87	+0.07

In this case, to 10 ml of $CuSO_4$ solution containing 0.25 g of metal was added a few drops of saturated solutions of ferric chloride and aluminum chloride; this was followed by the standard beryllium sulfate solution, 15-20 ml of a 15% solution of Complexone III,• 10 ml of water and 40 ml of a 2% alcoholic solution of ß-hydroxy-α-naphthoic aldehyde. The solution obtained was heated to 70° and then a 10% ammonia solution added gradually while the whole was stirred vigorously with a glass rod, until a yellowish turbidity appeared which almost immediately changed into a crystalline precipitate; the solution thereupon became emerald green in color. After 30 minutes the precipitate was transferred quantitatively to a No. 2 or No. 3 glass filter, washed 3 times with 50% alcohol and dried at 110° to constant weight. Analytical results are given in Table 4.

TABLE 5

Determination of Beryllium in Beryllium Bronze (sample weight 0.15 g)

Weight of the beryllium complex of ß-hydroxynaphthoic aldehyde	Beryllium found	
	in mg	in %
0.0886	2.27	1.52
0.0920	2.36	1.57
0.0892	2.29	1.53
0.0917	2.35	1.57

TABLE 6

Determination of Beryllium in Beryllium Bronze (sample weight 0.15 g) with Addition of Beryllium Salts

Beryllium added in mg	Beryllium found in mg	In the sample in mg	In the bronze in %
0.95	3.27	2.32	1.55
0.95	3.33	2.38	1.59
1.90	4.31	2.41	1.60
1.90	4.32	2.42	1.61

For the Determination of Beryllium in Beryllium Bronze 0.15 g of bronze was dissolved on heating in nitric acid (1:1); ammonia was then added until a precipitate formed followed by a few drops of concentrated hydrochloric acid until a clear solution was obtained. To this solution was added 7-8 ml of a 15% solution of

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• To 15 g of Complexone III was added a small amount of water until a pasty mass was obtained; concentrated ammonia solution was then added dropwise until the precipitate dissolved, and then water added to bring the volume up to 100 ml. The solution obtained was filtered, and concentrated hydrochloric acid added until methyl red used as indicator turned rose.

Complexone III, and water in such amount that after addition of 25 ml of an alcoholic solution of β-hydroxynaphthoic aldehyde, the solution contained 50% alcohol. The rest of the procedure was the same as that used for mixtures of the salts.

Results are given in Table 5.

For determination of beryllium in bronze with addition of beryllium salts, the results given in Table 6 were obtained.

It is evident from Table 6 that the method gives satisfactory results, and that experimental error for beryllium determination does not exceed permissible limits.

SUMMARY

1. A new quantitative method for determining beryllium by precipitating it with β-hydroxy-α-naphthoic aldehyde has been developed.

2. Beryllium determination can be carried out in the presence of elements which accompany it in beryllium bronze, by using Complexone III as masking agent.

3. The small conversion factor for beryllium (0.02565) means that during alloy analysis, small samples can be used.

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VARNISH RED C — A NEW INDICATOR FOR THE COMPLEXONOMETRIC DETERMINATION OF CALCIUM

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Murexide (ammonium purpureate) which was proposed by Schwarzenbach and Gysling [1], for colorimetric determination of calcium, has been used as the indicator for determination of calcium in pure solutions, or in the presence of magnesium, by the complexonometric method which has been widely applied during recent years.

The numerous published variants of the use of murexide as indicator or reagent for colorimetric determination of calcium [2-15], are characterized by the essentially small differences in the conditions employed.

The use of murexide during complexonometric determination of calcium is based on the following mechanism. Calcium, like all other elements, whose cations hydrolyze with difficulty, is capable of reacting with complexones in alkaline media. Since calcium cations hydrolyze less readily than those of magnesium, on gradually increasing the alkalinity, in accordance with considerations advanced previously [16], after attaining a certain concentration, the magnesium complex breaks down, while the calcium complex still remains intact. Titrations are therefore carried out under such conditions of alkalinity that magnesium is present as the hydroxide.

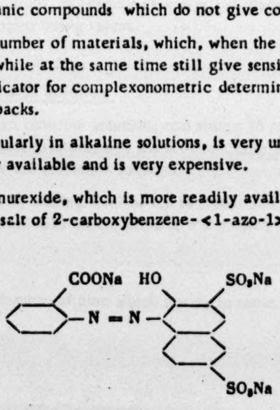
This permits determination of calcium, in the presence of magnesium, with good results, as long as there is not too much magnesium that it is difficult to titrate the precipitate of its hydroxide.

An indicator which is suitable for complexonometric determination of calcium, when the color reaction for calcium is sufficiently sensitive and contrasting, should not, at the same time, give a color reaction with magnesium. The latter condition is not easily satisfied. As noted elsewhere [19], as a result of the inherent capacity of magnesium hydroxide to adsorb many colored compounds leading to sharp changes in their color, it is not easy to select colored organic compounds which do not give color reactions with magnesium.

Murexide is one of a small number of materials, which, when the solution is alkaline enough, do not react with magnesium hydroxide, while at the same time still give sensitive and contrasting color reactions with calcium. Murexide as an indicator for complexonometric determination of calcium, however, still possesses a number of important drawbacks.

Murexide, in solution, particularly in alkaline solutions, is very unstable, and can only be stored as the solid; furthermore, it is not readily available and is very expensive.

A convenient substitute for murexide, which is more readily available than it, cheaper, and far more stable in solution, is the trisodium salt of 2-carboxybenzene-<1-azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid



The reagent is readily synthesized from diazotized anthranilic acid by coupling it with 2-hydroxynaphthalene-3,6-disulfonic acid (R-salt). Both starting materials are used in the aniline dye industry. The reagent itself is produced in large quantities commercially under the name "Varnish Red C" (TU MKhP No. 145-40) and is used for production of a widely used pigment (Tu MKhP No. 2268-50) which is the barium salt of this reagent containing other inorganic compounds.

At suitable pH values, which can be readily established on the basis of the general theory of the action of organic reagents [16], the recommended reagent gives color reaction with many elements; the colors which are formed are also in agreement with general theoretical propositions [18].

Calcium gives a normal color reaction, but on alkalization, like many other elements, readily gives a "blocking" color reaction (a color corresponding to the color of the reagent in acid media). In alkali media, reagent solutions have an orange-red color; calcium forms a yellow color. Reaction sensitivity which amounts to 10 γ/ml of Ca (when the color is observed in a volume of 100 ml), increases on adding alcohol or acetone (in 10% alcohol it increases to 5 γ/ml). In order to increase the contrast of the color transition during visual determinations, it is useful to add Methylene Blue as an internal light filter. Under the conditions used, magnesium, like some other elements, is precipitated as hydroxide, and does not give a color reaction.

Experimental procedure is the same for the new indicator as for murexide. The scope and limitations of the method are also the same in both cases.

Complexonometric Determination of Calcium Using Varnish Red C as Indicator

Reagents Required

1. Stock solutions for the indicator:

a) 0.35% aqueous solution of the sodium salt of 2-carboxybenzene- <1-azo-1> -2-hydroxynaphthalene-3,6-disulfonic acid (varnish red C);

b) 0.02% aqueous solution of Methylene Blue •;

c) a standard solution of calcium chloride containing 4 mg/ml Ca. 10.00 g of $CaCO_3$ (chemically pure) is dissolved in 110 ml 2 N HCl and diluted with water to 1000 ml.

Indicator solution is prepared by mixing 10 ml of solution a), 10 ml of solution b), about 5 ml of solution c), and 25 ml water. The amount of calcium added should be such that, after dilution with 0.1 N NaOH, the color which develops should correspond to the shade of the color formed when the reagent which gives the color reaction with calcium is half complexed by calcium.

The solution of indicator in 0.1 N NaOH acts as a reference which is used during titration of calcium, and for standardizing Complexone III with respect to calcium. The indicator solution is stable for an indefinite time.

2. 0.0200 and 0.100 M solutions of Complexone III ($C_{10}H_{12}O_8N_2H_2Na_2\cdot 2H_2O$:mol. wt. = 372.3; Trilon B). The solution is standardized with calcium, or reagent of analytical grade which can be used as a primary standard is used [17], the appropriate weights being taken.

3. 2.0 M NaOH solution.

Standardization of Complexone III Solution

To 3.25 ml of standard calcium chloride solution, containing 15 mg of Ca, is added 100 ml of water, 5 ml of 2.0 M NaOH, 1.0 ml of indicator solution, and the 0.02 M Complexone III solution titrated until the color of the solution corresponds to that of the reference solution.

Reference solution is prepared by adding 5 ml of 2.0 M NaOH and 1.0 ml of indicator to 100 ml water. The volume of the reference solution should be the same as the volume of the solution being titrated at the end of titration.

• It is necessary to check for the absence of zinc which occurs in some types of commercial Methylene Blue.

Determination of Calcium

(In the presence or absence of magnesium)

If the test solution is acid, it is roughly neutralized with 2 N NaOH using a small piece of litmus paper as indicator. 2 N NaOH is then added in an amount which is 1/20 of the expected final volume, and 1.0 ml of indicator solution added per 100 ml of the expected final volume; the whole is titrated with Complexone III until the color of the solution coincides with that of the reference solution.

Reference solution is prepared by adding to a volume of water which is equal to the expected final volume, 1/20th of its volume of 2N NaOH and 1.0 ml of indicator solution per 100 ml of solution. If calcium is determined in the presence of magnesium, some magnesium is added to the reference solution.

TABLE

Comparative Complexonometric Determination of Calcium with Murexide and Varnish Red C, respectively, as Indicators (solution volume 100 ml)

Taken in mg		Ca found in mg		Relative error in %		Mg taken		Ca found in mg		Relative error in %	
Ca	Mg	with murexide	with varnish red C	with murexide	with varnish red C	Ca	Mg	with murexide	with varnish red C	with murexide	with varnish red C
Titration with 0,020 M Complexone III						Titration with 0,100 M Complexone III					
1.7	—	1.8	1.6	+6	—6	14.7	—	14.9	14.6	+1.4	—0.68
3.1	—	3.2	3.3	+3.2	+6.5	14.7	5.0	14.3	14.3	+0.68	—2.7
3.1	3.0	3.1	3.2	0.0	+3.2	22.1	—	22.6	22.2	+2.3	+0.45
3.1	6.0	3.1	3.1	0.0	0.0	22.4	6.0	22.2	22.4	+0.45	+1.4
3.1	12,0	3,1	2.9	0.0	—6.5	22.1	12.0	22.2	22.2	+0.45	+0.45
3.1	25,0	3.0	3.0	—3.2	—3.2	22.1	25.0	22.0	21.9	—0.45	—0.90
3.1	50.0	2.7	2.6	—13	—16	22.1	50.0	21.2	21.4	—4.1	—3.2
3.6	—	3,7	3.8	+2.8	+5.5	31.4	—	31.3	31.2	—0.32	—0.64
7.0	—	7.1	7.2	+1.4	+2.9	60.8	—	61.3	60.9	+0.82	+0.16
15.2	—	15.3	15.2	+0.66	0.0						

Results for calcium determinations using murexide and varnish red C, respectively, as indicators, are given in the table. For determination of 1.5-60 mg of calcium in a volume of 100 ml, the new indicator is quite as good as murexide. Nevertheless, since the color reaction of calcium with the new indicator is less sensitive, during titration with 0.02 M Complexone III (using reference solution with a 50% color) a clear-cut change in color only occurs after the addition of 0.23 ± 0.03 ml of Complexone III solution, whereas in the case of murexide as indicator (also using a reference solution with a 50% color), a clear-cut color change is obtained after addition of 0.10 ± 0.02 ml of Complexone III.

When 0.100 M Complexone III is used for titration, a distinct color change is obtained in both cases, after addition of one drop of titrant. For calcium determination in the presence of magnesium, experimental error is approximately 0.2 mg, while in the presence of 50 mg magnesium, the error is 0.6 mg.

Synthesis of 2-Carboxybenzene-<1-azo-1> -2-hydroxynaphthalene-3,6-disulfonic acid

It is prepared by diazotizing anthranilic acid and then coupling the diazo compound formed with 2-hydroxynaphthalene-3,6-disulfonic acid (R-salt).

Diazotization. 2.74 g anthranilic acid (calculated on the 100% pure product) (0.020 M) is dissolved in 50 ml water on addition of 6 ml of concentrated hydrochloric acid, any contamination is filtered off, and the solution cooled; a few lumps of ice are added, and then, slowly, in the course of 5 minutes, a solution of 1.40 g of $NaNO_2$ in 20 ml of water added. The final volume is about 100 ml.

Coupling. 7.30 g of R salt, calculated on the basis of the anhydrous disodium salt (0.021 m), is dissolved in 50 ml water on addition of 4 g of anhydrous sodium carbonate, incidental contamination is filtered off, and the diazotized anthranilic acid slowly added to the filtrate with stirring. To the mixture obtained is added, over a 30 minute period, and with stirring, a filtered solution of 15 g of anhydrous sodium carbonate in 75 ml water, and the whole left for a few hours. The bright red product is filtered, pressed, washed with a little water, and removed from the filter funnel; for purification it is dissolved with slight heating in about 500 ml water. From the solution obtained, the product is thrown out by dropwise addition, with stirring, of 70 ml concentrated hydrochloric acid; the material is filtered, it is then washed with a little water, and dried on a table; the yield of the bright red product is about 8 g.

On completion of this work, it was learned on receipt of the April issue of Anal. Chem. for 1956, from a review by M. G. Mellon and D. F. Boltz (p. 562) that T. Ashizawa [Repts. Balneol. Lab. Okayamo Univ., 3,39-42 (1950); 6, 15-19 (1952) had recommended 2-carboxybenzene <1-azo-1->-2-hydroxynaphthalene-3,6-disulfonic acid for photometric determination of calcium.

H. Diehl and J. L. Ellingboe [Anal. Chem. 28, 882 (1956)]for complexonometric determination of calcium in the presence of magnesium, recommend "Calcein" as indicator (this is a product obtained from fluorescein, iminodiacetic acid, and formaldehyde).

SUMMARY

Varnish Red C (Lacquer Scarlet 3B)(2-carboxybenze- <1- azo-1>-2-hydroxynaphthalene-3,6-disulfonic acid, is proposed as a substitute for murexide in the complexonometric determination of calcium. In contrast to murexide, the new indicator is completely stable in solution; further, it is more readily available and cheaper.

Experimental procedure is identical to that used with murexide. For calcium determination in the presence of magnesium, titration is carried out in 0.1 N NaOH. Experimental accuracy for determination of more than 3 mg of calcium in 100 ml of solution is the same as for determinations involving murexide.

The indicator forms orange-red solutions, calcium gives a yellow color.

In order to improve the contrast of the color change, Methylene Blue is added to the indicator as an internal light filter.

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THE USE OF TETRAFLUOBORIC ACID IN QUANTITATIVE ANALYSIS

1. GRAVIMETRIC DETERMINATION OF ALKALI METALS IN BORATES, HALIDES, NITRATES, AND NITRITES

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Tetrafluoboric acid is readily formed on mixing boric acid with hydrogen fluoride [1]; it is a strong acid. Although HBF_4 is only known in solutions whose boiling points are sufficiently high to ensure expulsion of hydrogen halides, HNO_3, volatile organic acids, etc., excess HBF_4 is completely removed on taking the solutions to dryness. Many tetrafluoborates are fairly thermally stable. Data on the dissociation pressures of the tetrafluoborates of Na, K, Rb, and Cs (see [2]) relate to the molten salts and do not permit evaluation of the stability of solid salts, especially, since during these determinations, change in composition of the fused salts was not controlled. Nevertheless, according to other results [3], the weight of KBF_4 does not change up to 410°. It would be reasonable to expect that $RbBF_4$ and $CsBF_4$ are relatively stable, while $NaBF_4$, and particularly $LiBF_4$, should decompose at lower temperatures. Actually, according to Klinkenberg's results [2], the dissociation pressure of $LiBF_4$ is 760 mm at 324°.

We found that difficulties arise during determination of lithium as $LiBF_4$. Nevertheless, $NaBF_4$ is completely stable at 200°. Weighing as the tetrafluoborates has already been used successfully by one of us for the determination of potassium in complex fluoborates [4], and of sodium in $NaBF_4$ solutions [5].

In the work described here it is shown that the halides, nitrates, nitrites, and borates of Na, K, and Cs can be converted into tetrafluoborates much more readily than into sulfates. Presumably, rubidium salts should behave similarily. During analysis of borates and fluoborates there is no need to carry out the difficult separation of boron. The high equivalent weight of BF_4^- increases analytical accuracy. As will be shown in a subsequent article, the appreciable difference in the equivalent weights of BF_4^- and Cl^- permits one to achieve satisfactory accuracy during indirect determination of K and Na mixtures, by weighing as chlorides and tetrafluoborates; by making use of differences in solubilities of the tetrafluoborates, it is possible to separate Li and Na from K, Rb, and Cs. These advantages completely compensate for the necessity of using platinum crucibles for evaporation with HBF_4. Duration of evaporation to dryness and drying, probably, can be shortened (particularly in the case of K, Rb, and Cs salts) by using higher temperatures and cutting down sample weights.

EXPERIMENTAL

1. Effect of HF/H_3BO_3 Ratio on Volatility of the Acid

Aliquots of mixtures of chemically pure 40% HF and H_3BO_3 with initial molar ratios for HF/H_3BO_3 of 4, 3.5, 3.15, and 2.5 were evaporated in platinum crucibles on an air bath, and then dried at 140-150° to constant weight (1-1.5 hours). The first three mixtures were evaporated quantitatively, while in the case of the last mixture, there remained a small amount of nonvolatile residue (0.6 mg from 7.911 g of mixture, and 0.7 mg from 10.069 g mixtures, i.e., an average of 0.073 mg per g of mixture. These tests show that there is no need to fear the possibility of contamination of the tetrafluoborates formed, by H_3BO_3 or borates as a result of hydrolysis of HBF_4. Even with a known excess of H_3BO_3 in the original acid, it volatilizes completely; presumably, formation of volatile hydroxyfluoro compounds of boron occurs (hydrates of boron fluoride, dihydroxyfluoboric acid $H[BF_3(OH_2)]$, etc.). In subsequent experiments, the tetrafluoboric acid used was obtained by adding the theoretical amount of H_3BO_3 (1 mole to 4 moles of HF) to 40% hydrogen fluoride, "pure" grade, contained in a platinum dish cooled externally. In view of the appreciable exothermal nature of the reaction, H_3BO_3 was added in small portions. The acid prepared thus was stored in paraffined vessels. Evaporation of all test salts with HBF_4 was carried out in platinum crucibles; before addition of HBF_4, the test salt was dissolved in the minimum possible amount of water. All experimental results were corrected periodically for insignificant amounts of nonvolatile residue (from 0.3 to 0.36 mg per 2 ml of acid).

2. The Thermal Stability of $LiBF_4$

When solutions of pure grade Li_2CO_3 and HBF_4 were evaporated without sufficient care, an appreciable decrease in weight was observed (up to 4% of the theoretical weight of $LiBF_4$). When evaporation was carried out with greater care, decomposition of $LiBF_4$ was avoided, removal of residual HBF_4 by drying at 110-120°, however, was accompanied by insignificant decomposition of $LiBF_4$. Thus, after drying over periods of 1.5, 3, and 4 hours respectively, instead of 668.7 mg of $LiBF_4$, the following amounts were respectively obtained: 668.7, 664.7 and 663.6 mg. In a parallel series, instead of 645.9 mg, the following amounts were obtained 644.5, 643.4, and 642.9 mg, respectively. Calcining the samples gave the theoretical amount of LiF.

In another series of tests, the residues were weighed after drying at 120°, then after drying at 140 and 150° respectively (drying time at each temperature was 1 hour):

Theoretical weight $LiBF_4$ in mg	Weight of residue (in mg) after drying for 1 hour at		
	120°	140°	150°
268.8	270.1	268.4	265.9
388.7	390.6	389.6	386.6

Thus, drying the residue at 110-150° may lead to a lower accuracy (about 1%); but, conditions for lithium determination are less favorable than for other alkali metals.

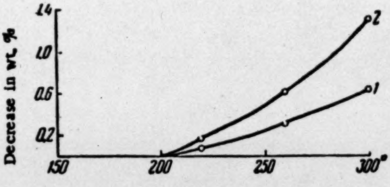
3. Thermal Stability of $NaBF_4$

Thermal stability of $NaBF_4$ was checked by heating 0.38-0.4 g of the salt at constant temperature and weighing the residue periodically.

TABLE 1

Loss in Weight of $NaBF_4$ on Heating

Experiment number	Temperature in °C	Duration of heating in hours	Loss in weight in %	
1	200	4	0.00	0.00
2	220	2	0.08	0.08
3	220	4	0.16	0.20
4	260	2	0.31	0.31
5	260	4	0.61	0.62
6	300	2	0.66	0.62
7	300	4	1.34	1.34



Decomposition of $NaBF_4$ on heating
1) Heating for 2 hours; 2) heating for 4 hours.

As is evident from Table 1, $NaBF_4$ is still quite stable at 200°. At 200°, very slow decomposition sets in, which accelerates on raising the temperature further (see diagram also); the percentage decomposition at each temperature is roughly proportional to duration of heating. The drying conditions which we used in all tests (170-175°), assure absence of any appreciable decomposition of $NaBF_4$.

TABLE 2

Determination of Sodium Borax, Sodium Fluoride, and Their Mixtures

Experiment number	Taken in mg		Weight of $NaBF_4$ in mg		Deviation	
	$Na_2B_4O_7 \cdot 10H_2O$	99.54% NaF	Theoretical	Found	In mg	In %
1	288.5	–	166.1	166.2	+0.1	+0.07
2	298.0	–	171.6	171.5	−0.1	−0.07
3	361.9	–	208.4	208.9	+0.5	+0.25
4	383.8	–	221.0	221.4	+0.4	+0.24
5	–	131.3	341.8	341.7	−0.1	−0.03
6	–	131.4	342.1	342.0	−0.1	−0.03
7	–	132.3	341.8	341.8	0.0	0.00
8	594.7	100.5	604.6	604.1	−0.5	−0.08
9	535.6	66.0	480.3	480.9	+0.6	+0.12
10	331.3	96.4	441.6	441.8	+0.2	+0.05
11	295.0	142.3	540.3	540.7	+0.4	+0.08

4. Determination of Sodium in Borax, Sodium Fluoride, and Their Mixtures, and of Potassium in Pentaborate

For determination of sodium in borax and other sodium borates in which the ratio B/Na is greater than 1, it is sufficient to evaporate them with hydrogen fluoride, the HBF_4 being formed in situ during determination. Excess hydrogen fluoride does not interfere (see below). Borax was purified and tested by the methods specified for preparing borax as a primary standard in acidimetry [6]; aliquots were evaporated on an air bath with an insignificant excess of HF (2 ml of 40% acid), and then dried in a drying oven at 170-175° to constant weight. Duration of evaporation until cessation of evolution of acid fumes was 1.5-2 hours. Drying for 1 hour proved sufficient in all cases. A replicate weighing (for control purposes) was made after drying for a further 30 minutes. A second treatment of the dried residue with fresh HF did not lead to appreciable change in weight. The results given in Table 2 confirm that a single evaporation with HF is sufficient to convert borax quantitatively into $NaBF_4$. The $NaBF_4$ obtained did not give a titer with alkali in the cold, thereby showing the absence of hydroxyfluoborates or $NaHF_2$ as impurities.

Sodium fluoride contained 99.54 ± 0.02% NaF (as determined by the sulfate method). A single evaporation with excess HBF_4 quantitatively converted it into $NaBF_4$ which was weighed after drying at 170-175° (Table 2); during calculation of the theoretical weight of $NaBF_4$, the percentage content of NaF in the original product was taken into account. Excellent results were obtained also during analysis of mixtures of borax and NaF. The mixtures in experiments 8 and 9, in which the ratio of B/Na was greater than 1, were evaporated with 2 ml of hydrogen fluoride. On evaporating mixtures of experiments 10 and 11, in which $B/Na < 1$, a small amount of H_3BO_3 was also added.

Since KBF_4 is less soluble and more thermally stable than $NaBF_4$, the method should be completely applicable also for potassium borates and fluorides. Results for determination of potassium in potassium pentaborate $KH_4B_5O_{10} \cdot 2H_2O$, which is readily obtained in a pure form, are given in Table 3. A second treatment with HF did not lead to change in residue weight. Probably, the fact that systematically high values were obtained is connected with slight efflorescence of the original material (0.25-0.36%).

TABLE 3

Determination of Potassium in Pentaborate

Experiment number	Weight of $KH_4B_5O_{10} \cdot 2H_2O$ in mg	Weight of KBF_4 in mg		Deviation	
		theoretical	found	in mg	in %
1	562.6	241.6	242.5	+0.9	+0.37
2	565.2	242.7	243.6	+0.9	+0.37
3	584.5	251.0	251.6	+0.6	+0.24

5. Determination of Sodium and Potassium in Chlorides, Bromides, and Iodides, and of Cesium in Chloride

Potassium chloride, sodium chloride, potassium bromide, and potassium iodide were purified and tested according to methods laid down for preparing standards for argentimetry [6]. Sodium bromide and iodides, in view of their high hygroscopicity, were used in solution, the concentrations of which were established argentimetrically.

Results of these determinations (after a single evaporation with 2 ml of HBF_4, and drying at 170-175°) are given in Table 4. The weights found for the tetrafluoborates are in excellent agreement with theory. Only negligible traces of halide ions were found in the tetrafluoborates obtained.

TABLE 4

Determination of Alkali Metals in Chlorides, Bromides, and Iodides of the Alkali Metals

Original material		Weight of tetrafluoborate in mg		Deviation	
composition	weight in mg	theoretical	found	in mg	in %
NaCl	293.5	551.5	551.8	+ 0.3	+0.05
NaCl	261.7	491.7	492.6	+ 0.9	+0.18
NaCl	233.1	438.0	438.2	+ 0.2	+0.05
NaCl	232.7	437.2	436.7	— 0.5	—0.11
NaBr	524.0	559.5	559.7	+ 0.2	+0.04
NaBr	418.0	446.1	446.4	+ 0.3	+0.07
NaI	466.7	341.9	340.9	— 1.0	—0.29
NaI	288.6	211.4	210.7	— 0,7	—0.33
KCl	247.4	417.8	418.3	+ 0.5	+0.12
KCl	201.4	340.2	340.7	+ 0.5	+0.15
KBr	406.7	430.3	430.7	+ 0,4	+0.09
KBr	347.5	367.7	367.4	— 0.3	—0.08
KI	443.8	336.6	337.0	+ 0.4	+0.12
KI	428.9	325.3	325.0	— 0,3	—0.09
KI	363.2	275.4	276.3	+ 0.9	+0.32
KI	241.5	183.1	183.8	+ 0.7	+0.38

The ease of conversion of chlorides into tetrafluoborates corresponds fully to the slowness of the reverse process. During a single evaporation of a sample of about 0.45 g $NaBF_4$ with 2 ml concentrated HCl, it was observed that 2-5% was converted into NaCl. Even after four treatments with hydrochloric acid, 21-22% of $NaBF_4$ was converted altogether into NaCl. The less soluble and more thermally stable KBF_4 was even more resistant to the action of HCl – only 0.63% of a sample of KBF_4 (about 0.35 g), was converted into KCl on treating it twice with 2 ml concentrated HCl, and 1.06% on treating it three times with HCl. An aliquot of cesium carbonate ("pure" grade) was first converted into CsCl by evaporating it with HCl and drying it. The tared chloride was then evaporated with 2 ml of HBF_4, it was dried at 150-170° and then weighed as $CsBF_4$. The theoretical weight of $CsBF_4$ was calculated from the weight of chloride.

TABLE 5

Determination of Cesium in Chloride

Weight of $CsBF_4$ in mg		Deviation	
theoretical	found	in mg	in%
210.4	210.1	— 0.3	—0.14
203.3	204.0	+ 0.7	+0.35
200.8	200.3	— 0.5	—0.25
200.0	199.6	— 0.4	—0.20

The somewhat larger deviations (see Table 5) than in the case of NaCl and KCl are probably connected with insufficiently pure carbonate (on the basis of the chloride weight, it contained 97.7% of the original material) since complete dehydration of the chloride was also accompanied with difficulty.

6. Determination of Sodium and Potassium in Nitrites and Nitrates

Chemically pure $NaNO_3$ and KNO_3 were recrystallized three times and dried. Sodium nitrite was used in the solution*, the alkali metal content of which had been checked by the sulfate method. As the results given in Table 6 show, these salts also are quantitatively converted into the tetrafluoborates on one evaporation with 2 ml HBF_4.

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* On addition of HBF_4 to solid nitrite there was an extremely vigorous evolution of nitrogen oxides; HBF_4 was added to the nitrite solution dropwise.

TABLE 6

Determination of Sodium and Potassium in Nitrites and Nitrates

Original material		Weight of tetrafluoborate in mg		Deviation	
composition	sample weight in mg	theoretical	found	in mg	in %
$NaNO_2$	344.3	548.0	548.6	+ 0.6	+0.11
$NaNO_2$	190.2	302.7	302.5	— 0.2	—0.07
$NaNO_3$	502.9	649.7	650.0	+ 0.3	+0 05
$NaNO_3$	390.3	504.2	504.8	+ 0.6	+0.12
$NaNO_3$	344.2	444.6	445.1	+ 0.5	+0.11
KNO_3	446.3	555.8	556.4	+ 0.6	+0.11
KNO_3	437.8	545.3	545.6	+ 0.3	+0.05
KNO_3	434.5	541.1	541.0	— 0.1	—0.02
KNO_3	301.1	375.0	375.6	+ 0.6	+0.16

SUMMARY

1. Mixtures of HF and H_3BO_3 evaporate completely as long as the molar ratio HF/H_3BO_3 exceeds 2.5.

2. $LiBF_4$ decomposes only very slowly at 110-150°. $NaBF_4$ is completely stable at 200°, and decomposes very slowly at 220°.

3. It has been shown that it is possible to convert fluorides, chlorides, bromides, iodides, nitrates, nitrites, borates, and mixtures of the borates and fluorides of the alkali metals (apart from lithium) quantitatively into tetrafluoborates.

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* T.p. = C. B. Translation pagination.

PARTITION CHROMATOGRAPHIC SEPARATION OF SODIUM AND POTASSIUM DURING GLASS ANALYSIS

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Sodium and potassium are usually determined in glasses of complex composition by a method [1, 2], which involves isolation of total alkali metals, followed by determination of the potassium content by the chloroplatinate or cobaltinitrites methods respectively; sodium is determined by difference. This method of successive separation of the components from alkali metals involves the use of an appreciable number of reagents, several filtrations, and evaporations; it is very laborious, and requires a high degree of skill on the part of the analyst. Moreover, since sodium is determined by difference, all the errors in preceding stages are summed up. Accordingly, it is very desirable to increase the accuracy of the method or, at least, lessen the difficulties, and cut down the time taken to carry out an analysis.

In recent years the technique of ion-exchange chromatography has found wide application for isolating alkali metals from various complex mixtures (cations and anions) and for their separation.

Removal of total alkali metals from multivalent cations is mentioned in several papers; in view of the significant difference in properties of alkali metals and multivalent cations, the problem is comparatively simple and can be solved both by displacement elution [3-5], and by the use of complexing agents [6-8].

Chromatographic separation of alkali metals on ion-exchange resins by displacement elution was first suggested by W. Cohn and H. Kohn [9]. The authors established that on washing a column of Dowex-50 in the H-form at a slow rate with dilute hydrochloric acid, chromatographic separation of alkali metals is effected. This method has been used and improved by many other authors. Kayas [10, 11], used it for separating alkali metals on Amberlite IR-100; Jentzsch and Frotscher [12], on Wofatite KPS-200; Wickbold, on Wofatite KS [13]; Beukenkamp, Rieman [14], succeeded, using this method, in separating sodium, potassium, and magnesium quantitatively, and applied it for silicate analysis [14]. All these investigations were carried out with sulfonated ion-exchange resins. Bregman and Murata [15], established that phosphate and phosphorylated resins exhibit enhanced selectivity with respect to alkali metals. Tooper, D'Amice, and Bregman [16], successfully used resins in the phosphate form for separating sodium and potassium in physiological solutions. Since only lithium and sodium of the alkali metals are capable of forming, really, very unstable complexes, Buser [17], used uramyldiacetic acid for separating lithium, sodium, and potassium on a cation-exchange resin; Nelson [18], used ethylenediaminetetracetic acid for the separation of the same mixture on an anion-exchange resin (in the ethylenediaminetetracetate form).

Two possible techniques are applicable to glass analysis:

1) Chromatographic separation of total sodium and potassium with subsequent chemical or chromatographic separation of these two;

2) Direct partition chromatographic separation of sodium and potassium.

For glass analysis (see Table 1) the method of displacement elution on a cation exchange resin was used both for separating sodium and potassium, after a preliminary separation of these metals from other cations, and for partition separation of sodium and potassium from their mixtures with the main components of the glasses.

TABLE I

Types of Glasses Analysed

Oxides	Type of glass			Oxides	Type of glass		
	ZS−4	S−88−8	S-88-13		ZS−4	S-88-8	S-88-13
SiO_2	55.3	61.7	69.5	MgO	—	—	3.5
B_2O_3	—	2	2	Na_2O	3.8	7.6	11
BaO	—	11.4	2	K_2O	9.2	7.6	6
CaO	—	1.5	5.5	ZnO	—	7.0	—
Al_2O_3	1.7	1.2	—	PbO	30	—	—

An aliquot of glass was decomposed as usual with a mixture of sulfuric and hydrofluoric acids, the silicon being removed as SiF_4. Excess HF was removed by evaporation, the dry residue was calcined, and then treated with distilled water, the solution was finally filtered free of insolubles (sulfates, basic salts, and oxides) [19]; the eluate was evaporated to 3-4 ml and fed into a column of cation exchange resin. The resin had been converted beforehand into the H-form by treatment with 2 N hydrochloric acid, and then washed with distilled water.

Chromatographic separation was controlled by means of radioactive indicators and the electroconductivity of the eluate [13]. When the latter method was used, separation was followed by comparing the electroconductivity of eluate and eluant respectively; a galvanometer with a germanium rectifier was used as null instrument. The content of the alkali metals in the eluate was determined gravimetrically: to a test fraction of eluate was added concentrated sulfuric acid, the solution evaporated to dryness and the residue of sulfates weighed.

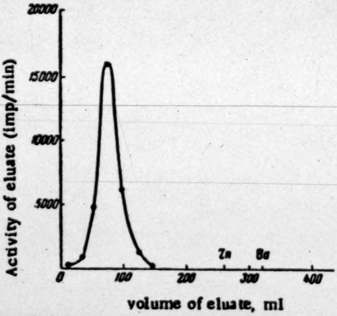

Fig. 1. Elution curve for sodium and potassium.

In order to obtain more exact conditions for separating total sodium and potassium, preliminary experiments were carried out on synthetic mixtures containing 1.25 mg $Al(NO_3)_3$, 77.5 mg $BaCl_2$, 58.7 mg $ZnCl_2$, 35.8 mg NaCl, 30.1 mg KCl (these correspond roughly to the contents of these cations in glass Type S-88-8) and the radioactive isotopes Na^{24} and K^{42}. Although isolation of total alkali metals, in view of the appreciable differences in absorbability of differently charged ions, can be carried out on any sulfonate type cation-exchange resin, in the present instance the cation-exchange resin RF was used. The column (d = 12.5 mm, h = 700 mm, 40 g cation-exchange resin RF) was washed with dilute hydrochloric acid, the activity of the eluate measured and an elution curve constructed. The presence of other cations in the eluate was established by well known qualitative reactions. Aluminum was not detected in 500 ml of test eluate. The elution curve obtained when the column was washed with 0.20 N HCl at the rate of 0.3 ml/minute, is shown in Fig. 1, on which are marked the volumes of eluate at which zinc and barium appeared.

As is evident from Fig. 1, in view of the large differences in sorbability of the alkali metals on the one hand, and the di- and tri- valent cations on the other, the latter do not appear in the eluate until significantly later than sodium and potassium. Such a large difference in behavior of sodium and potassium on the one hand, and of the remaining components of glass, on the other, means that one can elute total sodium and potassium at a high rate. Thus, at a rate of 0.7 ml/minute, qualitative analysis showed complete absence of di-and trivalent cations in 50 ml of the eluate obtained after removal of sodium and potassium.

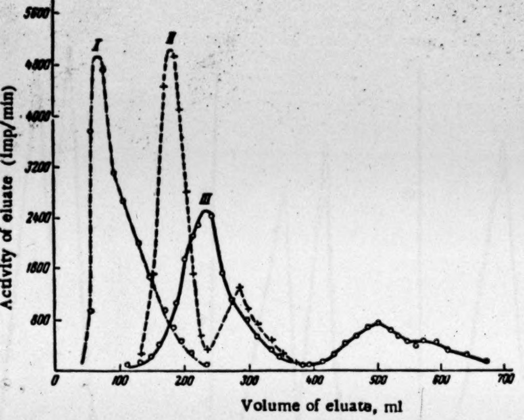

Fig. 2. Elution curves for sodium and potassium on various sulfonated resins.
I) SBS; II) SDV-1; III) KU-2.

For glass analysis, a column of the same dimensions and containing the same amount of resin was used. Total sodium and potassium were isolated by eluting the column at a rate of 0.7 ml/minute with 0.20 N HCl. Total sodium and potassium isolated as described by this chromatographic method can then be separated chemically or chromatographically. In the first instance one could, for example, determine potassium by means of chloroplatinate or cobaltinitrite; if this method is used, the advantage of the chromatographic method is limited to simply speeding up isolation of sodium and potassium from the original mixture, while determination of sodium is still carried out by difference. In view of the obvious advantages of the second method (chromatography), it was decided to separate total sodium and potassium chromatographically also. For this purpose we used the technique of partition chromatographic analysis of sodium and potassium by displacement elution of the column with dilute HCl; this technique is well known and has been checked by many foreign research workers. In this case the quality of separation is determined primarily by the selectivity of the resin. Since there is no published information on chromatographic separation of sodium and potassium on resins of Russian make, we started with a study of the selectivity of a number of Russian cation-exchange resins with respect to the alkali metals. Of the resins tested, the best one for separating the alkali metals proved to be the cation-exchange resin RF;* this was obtained by polycondensation of mono-resorcinol phosphate with formaldehyde [20], and confirms the statement [15] that resins with phosphate and phosphite active groups exhibit enhanced selectivity with respect to the alkali metals. All the same, the reverse order of elution of the alkali metals as compared with sulfonated cation-exchange resins, suggested by Bregman was not observed in our experiments. On tested sulfonated cation-exchange resins, separation of alkali metals was worse. As an example we have given the elution curves of sodium and potassium on the sulfonate resins KU-2, SDV-1, and SBS, which were obtained with the help of radioactive indicators.

Into a column (d = 12 mm, h = 300 mm, 10 g resin in the H-form) was introduced 50 mg each of NaCl and KCl and the radioactive isotopes Na^{24} and K^{42}. The column was eluted with 0.20 N HCl. 20 ml portions of eluate were selected. The activity of each fraction was measured with a γ-counter. The results obtained are given in Fig. 2.

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* This resin was synthesized in the Department of High Molecular Weight Compounds of the D. I. Mendeleev Moscow Chemicotechnological Institute and was kindly placed at our disposal.

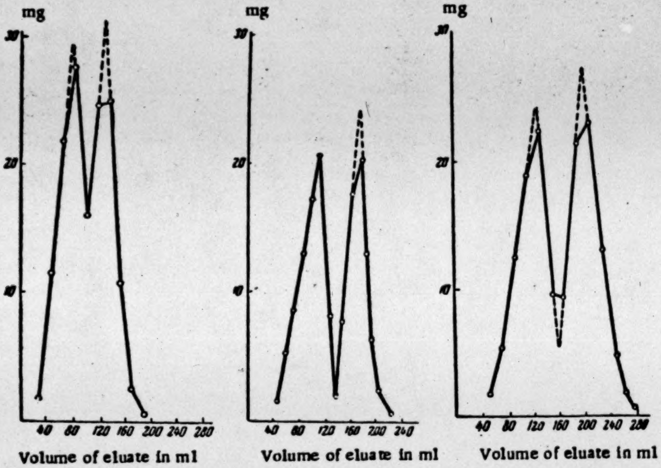

Fig. 3. Elution curves for sodium and potassium on cation-exchange resin RF on elution of the column with
a) 0.12 N HCl; b) 0.10 N HCl; c) 0.08 N HCl

It is clear from Fig. 2 that there is practically no separation of sodium from potassium on SBS; separation is observed on KU-2 and SDV-1, but the elution curves of the components cross each other somewhat; on RF, on the other hand, the separation effected is, comparatively, more clear cut. Experimental results obtained for separation of sodium and potassium on cation exchange resin RF (15 g resin, d = 12 mm, h = 300 mm), by eluting with hydrochloric acid solution of different concentrations (at a rate of 0.3 ml in 1 min per cm^2), are given in Fig. 3. It is clear that separation of sodium and potassium is better on washing the column with 0.10 N hydrochloric acid, and is quantitative when the right column length is used.

Glasses of types ZS-4, S-88-8, and S-88-13 were analyzed in this way.

As the results given in Table 2 show, those obtained by chromatographic analysis are in completely satisfactory agreement with those of chemical analysis. When glass is analyzed in this way by a chromatographic technique, owing to the simplicity of the latter, analysis becomes less laborious and requires less time to carry it out.

In a search for methods of cutting down further the time taken to carry out an analysis, a study was made of the possibility of direct partition chromatographic separation of sodium and potassium from their mixture with the main components of glass, without preliminary separation of these components. Separation was effected on RF cation-exchange resin (40 g, d of column 12 mm). The glass was treated by the method described above before chromatographic separation. Sodium was chromatographically separated by eluting the column with 0.10 N hydrochloric acid at a rate of 0.3 ml/minute, while potassium was removed by eluting the column with 0.20 N hydrochloric acid at the rate of 0.7 ml/minute. Under these conditions sodium was eluted with 250-300 ml of 0.1 N hydrochloric acid, while potassium was eluted with 100-120 ml of 0.2 N acid.

TABLE 2

Determination of Potassium and Sodium after Separating them from Other Components first, and then from each Other Chromatographically

Type of glass	Sample	After chromatographic separation in %			By the usual chemical method mean of several determinations in %		
		K_2O	Na_2O	K_2O+Na_2O	K_2O	Na_2O	K_2O+Na_2O
ZS-4	1	7.62 7.56 7.85 7.63 7.75 7.81	5.13 5.16 5.29 5.41 5.23 5.06				
		Mean 7.70	Mean 5.21	12.91	8.21	5.31	13.52
	2	9.12 8.85 9.13	5.17 5.19 5.38				
		Mean 9.03	Mean 5.26	14.28	9.13	5.17	14.30
	3	8.56 8.43	5.52 5.38				
		Mean 8.50	Mean 5.45	13.95	8.64	5.14	13.78
	4	9.13	5.26	14.39	9.13	5.17	14.30
S-88-8	1	7.65 7.80	6.75 6.66				
		Mean 7,73	Mean 6.75	14.48	7.79	6.84	14.63
S-88-13	1	8.01 8.05	10.80 10.72				
		Mean 8.03	Mean 10.76	18.79	7.96	11.34	19.30
	2	5.72 5.56	11.62 11.75				
		Mean 5.64	Mean 11.68	17.32	5.39	11.96	17.35

It is clear from Table 3 that, even without preliminary separation of total alkali metals, sodium and potassium can be quantitatively separated from each other and from the remaining components of glass.

By leaving out the intermediate stage of separating sodium and potassium from the remaining components, the duration of an analysis is cut down by 1.5-2 days, while the laboriousness of the analysis also diminishes.

In order to evaluate the accuracy of alkali-metals determination by this method, a synthetic mixture was analyzed which contained all the components found in the three types of glass we have been concerned with, with the exception of SiO_2 and B_2O_3.

TABLE 3

Determination of Potassium and Sodium after Their Direct Partition Chromatographic Separation

Type of glass	Sample No.	After chromatographic separation in %			By the usual chemical method (mean of determinations) in %		
		K_2O	Na_2O	K_2O+Na_2O	K_2O	Na_2O	K_2O+Na_2O
ZS-4	1	8.52	5.08	13.60	8.64	5.14	13.78
	2	9.13	5.26	14.39	9.13	5.17	14.30
	3	7.56	5.16				
		7.62	5.30				
		Mean 7.59	Mean 5.23	12.82	7.98	5.34	13.32
	4	8.48	5.17	13.65	8.61	4.62	13.23
S-88-8	1	7.60	7.23				
		7.85	7.76				
	2	Mean 7.72	Mean 7.49	15.21	7.79	6.84	15.63
		7.82	7.02				
	3	7.91	7.14				
	1	Mean 7.86	Mean 7.08	14.94	7.79	6.84	14.63
	2	8.02	7.03	15.05	7.79	6.84	14.63
S-88-13	3	8.01	10.80	18.81	7.96	11.34	19.30
		6.11	11.96	18.07	6.17	12.17	18.34
		6.16	12.81	18.97	6.20	12.47	18.76

Composition of Mixture*

1. $Al_2(SO_4)_3 \cdot 18H_2O$	0.0981 g	5. $Pb(C_2H_3O_2)_2$	0.1279 g
2. $CaSO_4$	0.0619 g	6. ZnO	0.0250 g
3. $MgSO_4 \cdot 7H_2O$	0.0917 g	7. Na_2CO_3	0.0769 g
4. $BaCO_3$	0.0129 g	8. K_2CO_3	0.0660 g

It is clear from Table 4 that the relative error in determining potassium and sodium does not exceed 5.7%, while the mean relative error amounts to 3%.

TABLE 4

Determination of Potassium and Sodium in a Synthetic Mixture After Direct Chromatographic Separation

K_2SO_4 0.0833 g taken			Na_2SO_4 0.1031 g taken		
Found in g	Error in g	Relative error in %	Found in g	Error in g	Relative error in %
0.0830	−0.0003	−0.4	0.1055	+0.0024	+2.3
0.0837	+0.0004	+0.5	0.1090	+0.0059	+5.7
0.0811	−0.0022	−2.6	0.1091	+0.0060	+5.7
0.0838	+0.0005	+0.6	0.1068	+0.0037	+3.6
0.0800	−0.0033	−4.0	0.1000	−0.0031	−3.0
0.0804	−0.0029	−3.4	0.1024	−0.0007	−0.7
0.0881	+0.0048	+5.7	0.1032	+0.0001	+0.1
0.0824	−0.0009	−1.0	0.1028	−0.0003	−0.3
0.0802	−0.0031	−3.7	0.1030	−0.0001	−0.1
0.0880	+0.0047	+5.6	0.1025	−0.0006	−0.6
0.0837	+0.0004	+0.4	0.1025	−0.0006	−0.6
	Mean 0.0021	Mean 3		Mean 0.0021	Mean 2

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* The choice of the anions was arbitrary, since they are converted into sulfates on treatment with sulfuric acid.

SUMMARY

1. It has been shown that best results are obtained for separating sodium and potassium [illegible] the cation exchange resin RF (a resin made in Russia) containing phosphate groups is used.

2. Three variants have been described for determining sodium and potassium in glass, which are based on ion-exchange chromatography:

a) Chromatographic separation of total sodium and potassium from their mixtures with other elements, followed by gravimetric determination of potassium; sodium being determined by difference.

b) Chromatographic separation of total sodium and potassium from their mixtures with other elements, followed by chromatographic separation of sodium and potassium, and gravimetric determination of each.

c) Direct partition chromatographic separation of sodium and potassium from their mixtures with other elements, followed by gravimetric determination of each component.

3. The use of a chromatographic technique in each of these methods means that, in comparison with the usual chemical methods, it is possible to cut down on the time required to carry out an analysis, and to decrease significantly the laboriousness of the method. In most cases, presumably, the most expedient to use would be the third variant; the relative error of this method does not exceed 5.7%, while the mean relative error is 3%. This method is being used at the moment for glass analysis in the analytical laboratory of an electric lamp factory.

4. The chromatographic methods described for the separation of sodium and potassium from glass, could, presumably, be used for determining alkali metals in silicates.

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A POLAROGRAPHIC METHOD OF DETERMINING INDIUM

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The polarographic behavior of indium in various supporting electrolytes has been studied by many authors [1-5]. The half-wave potential for reduction of indium in 0.1 N perchlorate is equal to −0.95 v, while in a supporting electrolyte of 0.1 N sulfuric acid, it is −1.06 v [6]. Nevertheless, in these supporting electrolytes, the waves obtained are drawn out and irreversible, and cannot therefore be recommended for analytical purposes. In supporting electrolytes of deformed anions, and in particular in solutions of the halides— chlorides, bromides, and iodides–reduction is reversible, and the half-wave potentials in 0.1 N solutions are respectively −0.56 −0.54 −0.53 v [5]. With increasing halide concentration, the half-wave potential is displaced toward the negative side. The half-wave potentials for reduction of the cations In^{3+}, Cd^{2+}, Fe^{2+}, Pb^{2+}, Sn^{2+} and Tl^{+} in a supporting electrolyte of 1 N KCl or HCl, relative to the saturated calomel electrode [7], are respectively −0.597; −0.642; −1.3; −0.435; −0.35; −0.48 v. Fe^{3+} gives a diffusion current at zero potential.

These values indicate that Fe^{2+} ions and small amounts of Pb^{2+}, Sn^{2+}, and Tl^{+} should not interfere with indium determination when using HCl or KCl as supporting electrolytes. The presence of even small amounts of Cd^{2+} in solution should interfere with indium determination.

In a supporting electrolyte of 1 N solutions of bromides and iodides, $E_{1/2}$ for In^{3+} is equal to respectively −0.58 v, and −0.55 v, while for Cd^{2+} the values are −0.70 v and −0.74 v. Since the half-wave potential of indium is more positive than that of cadmium, then it should be possible to determine indium in the presence of cadmium. In such a case, the bromide would be preferable to the iodide for analysis of technical materials, since, on addition of iodide to acid solutions, iodine is liberated which would interfere with polarographing.

In Fig. 1 are shown polarograms for indium and cadmium when both are simultaneously present in a supporting electrolyte of 4 M KBr. From these polarograms it is clear that even at concentration ratios of indium to cadmium of 1/200, the indium wave can be measured with reasonable accuracy.

The diffusion current of indium is proportional to indium concentration in this supporting electrolyte.

Preparation of solution prior to taking polarograms basically, consists of separating indium from those impurities whose half-wave potentials in this supporting electrolyte are very close to that of indium. Where necessary, concentration of the test element should also be carried out.

The major difficulties in preparing a solution prior to taking polarograms when indium is to be determined in the normally employed supporting electrolyte of chloride are bound up with the necessity of removing cadmium.

The published methods for polarographic determination of indium in the presence of cadmium in test samples, can be divided into three methods which differ in principle:

a) removal of indium from cadmium;

b) determination of the total diffusion current In^{3+} and Cd^{2+} [13, 14] in a weakly acid medium; followed by the determination of the diffusion current in ammoniacal medium; the amount of indium is determined by difference;

c) increasing the difference between the half-wave potentials of indium and cadmium by selection of supporting electrolyte.

A number of methods have been suggested for separating indium and cadmium. The one most often used is precipitation of indium as the hydroxide by ammonia; cadmium remains in solution [8, 9]. Despite the apparent simplicity of the method, it has a number of essential drawbacks: filtration of large volumes of solutions, washing of bulky hydroxide precipitate. Moreover, complete separation of indium and cadmium is not effected, since cadmium is partially adsorbed by the hydroxides [10]. It has also been shown that indium hydroxide partly dissolves in ammonia solution [11, 12]. It has also been suggested that indium be separated from cadmium by extraction of indium with ether from its solution in 5 N HBr [15].

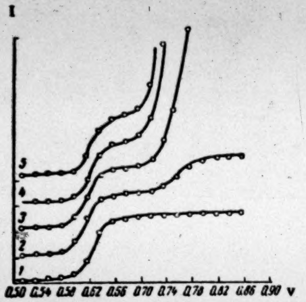

Fig. 1. Polarograms for indium and cadmium in 4N KBr at various ratios of indium and cadmium:
1) In : Cd = 1 : 0; 2) In : Cd = 1 : 1;
3) In : Cd = 1 : 20; 4) In : Cd = 1 : 100;
5) In : Cd = 1 : 200.

The methods indicated are rather cumbersome and are not always accurate enough (particularly in the presence of large concentrations of cadmium and low concentrations of indium). Since these published methods have the drawbacks mentioned, the necessity arose of developing a polarographic method of determining indium, which is sufficiently accurate and at the same time rapid, and allows, where necessary, for concentrating the indium before determination.

In preparing solution for polarographing, it must be taken into consideration that the ions Fe^{3+}, Pb^{2+}, Tl^{+}, Sn^{2+} and Cd^{2+}, and arsenic also, in concentrations of the same order as indium, interfere with determination of indium. In contrast to supporting electrolytes of chlorides, when polarograms are taken in supporting electrolytes of KI or KBr, cadmium does not interfere with indium determination, if the cadmium content is not more than 200 times that of the indium.

We used zinc oxide as suggested by Semerano for this purpose for separating indium and cadmium [18]. Cadmium hydroxide occurs considerably earlier in the pH_0* series than indium hydroxide. pH_0 for cadmium hydroxide is 6.84 [17], while pH_0 for indium hydroxide is 1.97**. Accordingly, by regulating the pH by means of zinc oxide, whose pH_0 is equal to 5.78, it is possible to precipitate indium hydroxide completely, leaving all the cadmium behind in solution. It should be noted that zinc oxide or hydroxide will not precipitate ferrous hydroxide, for which pH_0 is equal to 6.62. If zinc oxide is added to a solution containing indium and cadmium salts, the zinc oxide will dissolve and precipitation will occur of the hydroxides of metals which are lower in the pH_0 series than zinc hydroxide; indium hydroxide is included in this number. Cadmium, thallium, and ferrous ions remain in solution.

Tests showed that zinc oxide precipitates indium hydroxide from solution, while cadmium remains in solution (Fig. 2). The slight break around −0.7 v on polarograms of solutions of the precipitates obtained as described, is obviously the result of the presence of insignificant amounts of cadmium adsorbed by the precipitate. The amount of cadmium does not affect completeness of separation. During separation of indium in the presence of ferrous ions (10 g/liter), and copper (0.5 g/liter) at ratios of In^{3+} : Cd^{2+} ranging from 1 : 1 to 1 : 25, good results were obtained.

Indium is often found in small amounts in many technical materials, so that it is necessary to concentrate it before determination, taking large aliquots of sample for the purpose. Precipitation of indium hydroxide by means of zinc oxide with the aim of isolating it, can also be used for concentrating this metal.

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* pH_0 or normal pH is the equilibrium value of pH in a heterogenic system of metal hydroxide − metal salt − water, at a concentration of metal ions, equal to one mole.

** The value of 1.97 for the pH_0 of indium oxide was calculated by us from the value of the solubility product which was determined by a method described earlier [16].

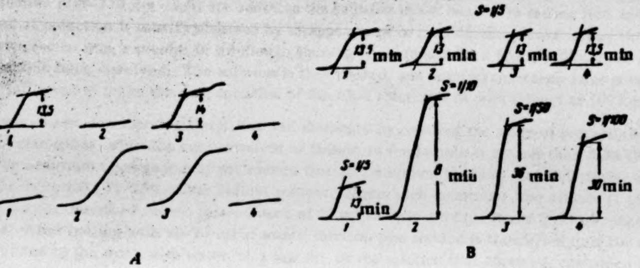

Fig. 2. Polarographic control of the separation of indium and cadmium by means of zinc oxide. Upper series ⌐indium waves after removal of cadmium from it; lower series ⌐cadmium waves in the filtrates:
A: 1) 1.6 mg/l In; 2) 2.0 mg/l Cd; 3) 1.6 mg/l In+2.0 mg/l Cd; 4) 0.1 N: B: 1) In:Cd = 1:1; 2) In:Cd = 1:10; 3) In:Cd = 1:30; 4) In:Cd = 1:50.

TABLE

Polarographic Determination of Indium in 4 m KBr

Indium taken in mg	Cadmium taken in mg	Indium found in mg	Relative error in %	Observations	Indium taken in mg	Cadmium taken in mg	Indium found in mg	Relative error in %	Observations
1.60	—	1.60	0.0	With separation	1.00	1	1.02	+2.0	Without separation
1.60	1.6	1.60	0.0		1.00	20	1.00	0.0	
1.60	20	1.66	+3.8		1.00	100	1.02	+2.0	
1.60	48	1.54	—3.8		1.00	200	1.04	+4.0	
1.60	80	1.60	0.0						

In the table are given results for polarographic determination of indium in a supporting electrolyte of 4 M KBr, in the presence of cadmium, both after preliminary isolation of indium by means of zinc oxide, and without such isolation.

The table shows that, in all cases, completely satisfactory results were obtained with a maximum relative error of 4%.

Analytical Procedure

An aliquot of test material is dissolved in a mixture of 50 ml sulfuric acid (1:3), 10 ml concentrated hydrochloric acid, and 0.2 g hydrazine sulfate (or hydrochloride), contained in a 250 ml beaker. The solution is evaporated almost to dryness on a sand bath; during this process the indium is partially freed from arsenic, selenium, and tellurium. After cooling, about 50 ml of water is added to the contents, the mixture brought to the boil and boiled for 10-15 minutes. The insoluble residue which remains after this process, and which contains silica, lead as sulfate, and some of the tin as basic salts, is filtered off, the filtrate is collected in a 500 ml beaker, it is then diluted with water to 200 ml, it is heated almost to the boil, and small amounts of well ground zinc oxide added until the solution gives a neutral reaction to Methyl Orange. A small excess of zinc oxide is then added and heating at the boil continued for a further 10 minutes. The precipitate is filtered off, washed with hot water and dissolved on the filter with hot hydrochloric acid (1:1).

This solution is evaporated on a sand bath to a small volume. Before completion of evaporation, small lumps of alumina (100-150 mg each) are added to the solution in the beaker to reduce iron and to remove arsenic. End of reduction is usually observed by disappearance or considerable weakening of the yellow color of the solution (when iron is present in solution). Heating is continued for a further 10 minutes after the last lumps of alumina have dissolved. The solution is then cooled, and polarograms taken after potassium bromide (in amounts sufficient to make the concentration of the final solution 4 M with respect to it*) has been added.

Analysis can be considerably simplified and shortened by omitting the stage of precipitating indium hydroxide with zinc oxide when the concentration of indium in the sample is greater than 0.1% (in solution ~0.1 g/liter). The cadmium content should not exceed that of the indium by more than 200 times, while thallium should not be more than 10-15% of the indium content. Under such conditions, the aliquot (1 g) is dissolved in the same way as described above, in a mixture of 20 ml sulfuric acid (1:3) and 5 ml of concentrated hydrochloric acid. After boiling with 20-25 ml of water, solution plus residue is transferred to a 100 ml standard flask, and diluted to the mark with water; to a few ml of the solution thus obtained, contained in a test tube, is added about 0.5 g of iron powder and the whole shaken for 2 minutes; iron cements the copper and arsenic, and reduces Fe^{3+} to Fe^{2+}, while oxygen is removed at the same time from solution.

Part of the solution from the test tube is filtered through a dry filter. Completeness of reduction is tested for by adding 1-2 drops of filtrate to 0.5 ml of 4 M KBr acidified with hydrochloric acid. The appearance of a yellow color because of the presence of Fe^{3+} in solution, testifies to incomplete reduction. If this should be the case, a further 0.5 g of iron powder is added to the solution in the test tube and the whole operation repeated. When addition of filtrate to an acid solution of potassium bromide does not lead to the appearance of a yellow color, or the color which develops is very weak, reduction can be regarded as complete. Usually a 2-4 minute shaking with iron powder is sufficient to get to this stage. When one is assured of complete reduction, an aliquot part of the filtrate obtained after filtration through a dry filter is taken for polarographic analysis. The supporting electrolyte is 4 M potassium bromide acidified with hydrochloric acid (1-2 drops of concentrated hydrochloric acid to 50 ml of potassium bromide solution).

SUMMARY

A polarographic method for determination of indium in the presence of cadmium has been developed. The method consists of concentrating and separating the indium with zonc oxide, dissolving the precipitate thus obtained in hydrochloric acid, and taking polarograms in a supporting electrolyte of 4 M potassium bromide.

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* When large amounts of copper are present, the solution, prior to taking polarograms, is shaken with iron powder.

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QUANTITATIVE DETERMINATION OF THALLIUM BY THE INTERNAL ELECTROLYSIS METHOD WITH PRECIPITATION OF TRIVALENT THALLIUM OXIDE ON THE ANODE

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The question regarding an accurate, rapid, and readily carried out method of determining thallium, despite many attempts at solving it, still remains open.

The internal electrolysis method, which leads to a partial solution of the problem, has been carried out on a setup which is a modification of one proposed earlier by A. Liptschinsky, B. Zagorev, and Khr. Sheutanov for determination of copper [1, 2], and zinc [3]. The apparatus is shown in Fig. 1. A sleeve covered with collodion, and containing a mixture of PbO_2 and dilute H_2SO_4, is connected with a Fischer electrode, and the whole immersed in a solution of a univalent thallium salt. Thallium oxide starts to deposit on the platinum electrode, since the value of the oxidation potential of the pair: $Tl_2O_3 + 6H^+/2Tl^+ + 3H_2O$ [4], is considerably lower than that of the pair: $PbO_2 + 4H^+ + SO_4^{2-}/PbSO_4 + 2H_2O$. The following process occurs on the cathode (PbO_2):

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e = PbSO_4 + 2H_2O, \qquad (1)$$

while on the platinum electrode, the process which takes place is:

$$2Tl^+ + 3H_2O - 4e = Tl_2O_3 + 6H^+ \qquad (2)$$

All experiments were carried out with two solutions of thallium sulfate prepared from Tl_2SO_4 obtained from Ciba (Basle, Switzerland). The concentrations of the solutions were established by the sulfate method: known volumes of the working solutions, acidified with sulfuric acid, were carefully evaporated in a platinum crucible and the residue heated in a double crucible at 600 ± 10° to constant weight. Results of duplicates were in good agreement: 20 ml of solution I contained 21.7 mg of thallium, while solution II contained 29.5 mg/20 ml.

Thallium was determined by the internal electrolysis method using the following conditions: 20 ml of the thallium salt solution contained in a 150 ml (diameter 5 cm) Jena glass beaker, was diluted with distilled water to 50 ml; in the solution was immersed the sleeve covered with collodion (external diameter 2.8 cm, height 8.0 cm), and which was three quarters full of PbO_2 and diluted H_2SO_4, mixed into a thick paste, and a platinum grid electrode (3.2 cm diameter and 3.0 cm height) connected with the PbO_2 as shown in Fig. 1.

The sleeve was prepared as follows. A cellulose thimble used for a Soxhlet apparatus, and with wall thickness 2 mm was immersed for 2 minutes in a 4% ethereal solution of collodion. After this immersion, the thimble was turned upside down, left to dry and then filled with PbO_2 and H_2SO_4. A sleeve prepared in this way can be used repeatedly for thallium determination; in the work described here, the same sleeve (without renewal of PbO_2 and H_2SO_4) was used for more than 50 thallium determinations, and during that time no changes in its character observed. As soon as the sleeve and platinum electrode are immersed in a Tl_2SO_4 solution, a black shining deposit of Tl_2O_3 is immediately formed tightly packed on the anode. The deposit dissolves with difficulty on heating in nitric acid (1 : 1). Such a deposit is formed during electro-analytical deposition of thallium on the anode [4-12]. Completeness of deposition of thallium was checked by adding a solution of Na_2S (there should be not more than a weak darkening of the solution).

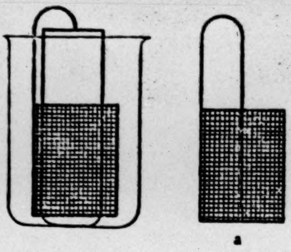

Fig. 1. Apparatus for thallium determination a) platinum electrode.

When thallium deposition was finished, the platinum electrode was withdrawn from the liquid and carefully washed, first with distilled water, and afterwards with ether; the electrode was then weighed. Contamination on the bent end of the platinum electrode (the end in the mixture of PbO_2 and H_2SO_4) was easily removed with a strong jet of water. Results for thallium determinations under various conditions are given in the table.

Addition of NH_4NO_3 led to an increase in the conductivity of the solution and to a speeding up of thallium deposition. During electrolysis, the solution temperature should be kept at 60-70°, since this accelerates Tl_2O_3 deposition. Complete deposition of 20-30 mg of thallium on the anode as Tl_2O_3 is complete after 30 minutes (Fig. 2), when 1.0 g of NH_4NO_3 is added to a test volume of 50 ml. It is best to let electrolysis take longer; e.g. 45 minutes, 59.0 mg of thallium can be completely deposited in 60 minutes.

Deposit composition did not change when electrolysis was carried out for longer periods (Experiments Nos. 25-27, 31, 32).

Since there is a published reference to contamination of Tl_2O_3 deposited on the anode by SO_4^{2-} [10], experiments were carried out to establish whether or not the deposits do in fact adsorb these ions. Tl_2O_3 deposits, accumulated after 20 determinations of thallium (about 0.66 g Tl_2O_3), were dissolved in HNO_3. The solution was evaporated to remove most of the HNO_3, it was then diluted with a small amount of water; on addition of a solution of $Ba(NO_3)_2$ to the solution thus obtained a weak opalescence of $BaSO_4$ was observed after one hour. This shows that the deposit of Tl_2O_3 only contains traces of SO_4^{2-}.

For the electro-analytical determination of thallium by anodic deposition of thallium it is stipulated that the electrode plus deposit should be heated at 160-170° to constant weight, in order to remove water [6,8]. In this connection, the following experiments were carried out: the tared electrode with the deposit of Tl_2O_3 on it was left in a drying oven at 165 ± 2° for 1 hour, after which they were weighed again. No changes in weight were observed.

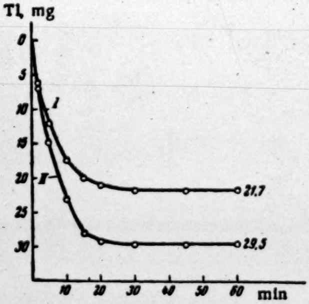

Fig. 2. Deposition curves for thallium.

Accurate results were also obtained for deposition of thallium from sulfuric acid solutions at pH 1.5 (experiments Nos. 15-17). The outward appearance and other properties of the deposit remained unchanged.

Ag^+ ions have no effect on accuracy of thallium determination. During determination of 21.7, 29.5, and 59.0 mg of Tl in the presence of 63.0, 630, 2520, and 3150 mg, respectively, of Ag for a total volume of solution of 50 ml, the following amounts of thallium were found: 21.8, 21.8, 29.5, 59.0, 59.2 mg Tl.

Quantitative determination of thallium in the presence of other ions is being studied at present. Under the conditions used for the technique developed, thallium can be determined in the presence of large amounts of Cd^{2+}, Zn^{2+}, etc. Thus, it is possible to determine thallium in such materials as metallic cadmium, zinc, etc.

TABLE

Experiment number	Tl taken in mg	Found in mg		Duration of electrolysis in minutes	Amount of NH_4NO_3 added in g	Other experimental conditions
		Tl_2O_3	Tl			
1	21.7	20.9	18.7	30	—	
2	21.7	21.8	19.5	60	—	At 20-22°
3	21.7	22.6	20.2	90	—	Solution was only heated to 60-70 at beginning of determination
4	21.7	22.8	20.4	30	—	Ditto
5	21.7	23.2	20.8	45	—	Solution maintained at 60-70 throughout *
6	21.7	23.8	21.3	60	—	
7	21.7	23.9	21.4	60	—	
8	21.7	24.3	21.7	30	2.0	
9	21.7	24.2	21.7	30	1.0	
10	21.7	24.3	21.7	30	1.0	
11	29.5	33.1	29.6	30	1.0	
12	29.5	32.9	29.4	30	1.0	
13	21.7	24.3	21.7	45	1.0	
14	21.7	24.3	21.7	45	2.0	
15	21.7	24.3	21.7	45	1.0	In sulfuric acid medium at pH 1.8
16	29.5	32.9	29.4	45	1.0	In sulfuric acid medium at pH 1.5
17	29.5	33.0	29,5	45	1.0	In sulfuric acid medium at pH 1.5
18	29.5	33.0	29.5	45	2.0	
19	29.5	33.1	29.6	45	1.0	
20	29.5	33.0	29.5	45	1.0	
21	21.7	24.4	21.8	60	1.0	
22	21.7	24.3	21.7	60	1.0	
23	21.7	24.3	21.7	60	1.0	
24	29.5	32.8	29.4	60	1.0	
25	29.5	33.0	29.5	210	1.0	
26	29.5	33.0	29.5	300	1.0	
27	29.5	33.0	29.5	720	1.0	
28	59.0	64.6	57.8	45	1.0	
29	59.0	66.0	59.1	60	1.0	
30	59.0	66.1	59.1	60	1.0	
31	59.0	66.0	59.1	75	1.0	
32	59.0	66.1	59.1	210	1.0	

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* This conditon was observed in all subsequent experiments.

SUMMARY

A rapid, accurate, and readily carried out method has been developed for quantitative deposition and determination of thallium.

The composition of the deposit corresponds to the formula Tl_2O_3; the deposite hardly adsorbs any SO_4^{2-}, and does not contain occluded water.

The presence of Ag^+ in solution, in amounts which are a hundred times that of the thallium, does not affect the accuracy of thallium determination.

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A NEW ANALYTICAL METHOD OF DETERMINING PROTOACTINIUM

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The properties of protoactinium, particularly its chemical properties, are still far from being thoroughly studied, since investigators are limited by the small amount of protoactinium isolated.

Protactinium exhibits a considerable tendency to hydrolyze, to form colloids, to form complexes, and to exhibit adsorption, all of which makes its separation from other elements, particularly from radioelements present in unweighable amounts in ores, very difficult.

Published methods for isolating protoactinium are cumbersome and complex. Analytical methods of determining protoactinium which would permit the protoactinium content of an ore to be established rapidly and accurately are unknown.

In addition, analysis of ores for their protoactinium content is of great interest for solving a number of geochemical problems, and also for controlling industrial processes of extracting protoactinium.

In developing a method for determining protoactinium, we have tried to find a selective precipitant, which ensures the isolation of this element both from weighable amounts of impurities, and from radiochemical contamination. Protoactinium is known to be best coprecipitated with zirconium compounds; accordingly, we tried out a whole series of selective zirconium precipitants: phthalic, phenylarsonic, and mandelic acids respectively.

TABLE 1

Coprecipitation of Protoactinium with Zirconium Mandelate from Nitric Acid Solutions

HNO_3 conc.	Duration		Pa isolated in %			
	of heating in minutes	of standing	for I precipitation	for II precipitations	for III precipitations	total
1:1	20	10 min	15	—	—	—
1:1	20	24 hours	25	17	35	77
1:2	20	1 hr	15	13	12	40
1:2	30	2 days	32	25	18	75
1:2	30	2 days	30	30	15	75
1:3	20	1 hour	15	10	10	35
1:3	30	24 hours	28	20	17	65
1:4	20	3 hours	32	20	15	67
1:5	20	3 hours	24	25	20	69

Tests showed that phthalic acid is not suitable for separating protoactinium, since only 60-70% of the protoactinium is coprecipitated with the precipitate of zirconium phthalate. Further, this technique does not allow one to separate protoactinium from polonium, purification from which presents the greatest difficulty.

The other selective precipitant for zirconium – phenylarsonic acid – coprecipitates 90-95% of the protoactinium with zirconium phenylarsonate. Nevertheless, in this case also, radiochemical purification during coprecipitation with zirconium phenylarsonate is not achieved, since up to 90% of polonium is precipitated with protoactinium.

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*Deceased.

Good results were obtained when madelic acid was used; this proved to be a successful precipitant for protoactinium, allowing it to be separated from α-active radioelements accompanying it.

In experiments carried out to develop a technique for the analytical determination of protoactinium, the indicator isotope Pa^{233} was used.

Coprecipitation of Protoactinium with Zirconium Mandelate

It is known that precipitation of zirconium with mandelic acid ensures good purification of zirconium from impurities. Mandelic acid $C_6H_5 \cdot CHOH \cdot COOH$ dissolves readily in alcohol and ether. The solubility of mandelic acid in water is 16g/100 g at 20°.

Tests on coprecipitation of protoactinium with zirconium mandelate in hydrochloric acid media gave good results. In nitric acid solutions, however, although conditions were varied, complete isolation of protactinium was not achieved (see Table 1). Accordingly, all tests in a study of the coprecipitation conditions of protoactinium with zirconium mandelate were carried out in hydrochloric acid solutions.

TABLE 2

Effect of Time of Heating of Solution on Coprecipitation of Protoactinium with Zirconium Mandelate

Heating time in minutes	Pa added in p.p.m	Pa isolated in p.p.m.	Completness of isolation
10	200	130	65.0
20	200	138	69.0
20	300	230	76.6
30	250	220	88.8
30	250	200	80.0
40	280	260	92.8
40	280	250	89.2
50	400	390	97.5
60	250	240	96.0
60	250	242	96.8

TABLE 3

Effect of Length of Time for which Precipitate is allowed to stand on Coprecipitation of Protoactinium with Zirconium Mandelate

Standing time of ppt.(hours)	Pa added in p.p.m.	Pa isolated in p.p.m.	Completness of isolation
1/3	250	130	52.0
1/3	300	165	55.0
1	280	158	56.4
2	300	188	62.6
3	200	142	71.0
5	250	200	80.0
20	280	268	95.8
20	300	273	91.0
20	280	260	92.8
20	250	233	93.2
20	250	228	91.2

In the search for optimum conditions for isolating protoactinium with zirconium mandelate precipitate from hydrochloric acid solutions, we varied the heating time of the solution, the time for which the precipitate was allowed to stand, the concentration of the zirconium carrier, and hydrochloric acid concentration (Tables 2-5).

A good yield of protactinium was obtained on heating the solution for one hour.

Completeness of isolation of protoactinium also depends on the time for which the precipitate is allowed to stand. As Table 3 shows, protoactinium is isolated with success on allowing the precipitate to stand for 20 hours.

At low zirconium concentrations, loss of protoactinium occurs (Table 4). Good results were obtained for concentrations of 10 mg zirconium /100 ml solution.

Completeness of separation of protoactinium does not depend on hydrochloric acid concentration (Table 5).

In subsequent experiments we settled on a hydrochloric acid concentration of 1 : 1, since it proved that at this concentration, maximum radiochemical purification of protoactinium was attained (Table 7 and 8).

On the basis of the results obtained, the following procedure was developed for coprecipitation of protoactinium with zirconium mandelate.

To 25 ml of solution containing protoactinium was added 25 ml of concentrated hydrochloric acid, 1 ml of zinc chloride solution (containing 10 mg Zr) and 50 ml of a 16% solution of mandelic acid. The mixture was heated on a water bath for 1 hour and left to stand for 24 hours. A white crystalline precipitate of zirconium mandelate separated out 10-20 minutes from the time when heating of the solution commenced. After 24 hours standing the precipitate was centrifuged and washed with alcohol. The washed precipitate was worked up with 5% alkali; it was then dissolved in a small volume of 6 N HCl and reprecipitated. Results for isolation of protoactinium are contained in Table 6.

TABLE 4

Effect of Concentration of Zirconium-Carrier on Coprecipitation of Protoactinium with Zirconium Mandelate

HCl concentration, N	Pa added in p.p. m	Pa isolated in p.p. m.	Completeness of isolation
1	320	248	77.5
2	300	250	83.3
3	300	250	83.3
4	280	252	89.9
5	250	218	87.2
6	250	223	89.2
10	200	185	92.5
10	200	187	93.5

TABLE 5

Effect of Hydrochloric Acid Concentration on Coprecipitation of Protoactinium with Zirconium Mandelate

Amount of Zr in mg/100 ml solution	Pa added in p.p. m.	Pa isolated in p.p. m.	Completeness of isolation
0.1	300	275	91.6
0.5	300	284	94.6
1	300	280	93.3
2	320	304	95.0
3	340	319	93.8
6	380	362	95.3
6	300	285	95.0
6	350	338	96.6

TABLE 6

Isolation of Protoactinium with Zirconium Mandelate Precipitate in in Hydrochloric Acid Media

Completeness of isolation of Pa in %			Completeness of isolation of Pa in %		
after one precipitation	after repeated precipitation	total after two precipitations	after one precipitation	after repeated precipitation	total after two precipitations
92	5	97	88	10	98
93	6	99	91	7	98
90	10	100	92	6	98
96	2	98	91	5	96
90	9	99	90	7	97
94	5	99	92	4	96

As the results given in Table 6 show, the method developed for coprecipitation of protoactinium with zirconium mandelate permits isolation of 90-95% of protoactinium after one precipitation, and up to 100% after two precipitations.

Next, we investigated whether or not mandelic acid is such a selective precipitant for protactinium as for zirconium, and whether or not, during coprecipitation of protoactinium with zirconium mandelate, radiochemical purification of protoactinium (from polonium, thorium, and radium) is achieved.

In order to check on the possibility of purification from polonium during coprecipitation of protoactinium with zirconium mandelate, the latter was precipitated from solutions containing a known amount of polonium, at various hydrochloric acid concentrations.

As can be seen from Table 7, at low hydrochloric acid concentrations, up to 40% of polonium is trapped by zirconium mandelate precipitate. With increasing hydrochloric acid concentration the amount of polonium decreases, and at HCl concentration of 1 : 1, the amount of polonium does not exceed 0.2%. Reprecipitation of precipitate allows one to separate protoactinium completely from polonium.

The possibility of purification from thorium isotopes during coprecipitation of protactinium with zirconium mandelate from hydrochloric acid solutions was studied with the aid of indicator UX_1.

TABLE 7

Purification from Polonium during Coprecipitation of Protoactinium with Zirconium Mandelate

HCl concentration, N	Po added in p.p.m	Po found in the precipitate	
		In p.p.m	In %
0.04	1000	380	38
0.04	1000	380	38
0.1	1200	325	27
0.1	1200	300	25
0.1	1200	325	27
6	2000	3	0.15
6	2000	3	0.15
6	2000	3	0.15
6	2320	4	0.17
6	2320	4	0.17
6	2320	5	0.21

TABLE 8

Purification from UX_1 during Coprecipitation of Protoactinium with Zirconium Mandelate

HCl concentration, N	UX_1 added in p.p.m.	UX_1 trapped by the precipitate	
		In p.p.m	In %
0.04	1000	770	77
0.04	1000	800	80
0.1	1200	1020	85
0.54	1200	792	66
1	800	480	60
3	800	30	3.7
6	2000	8	0.4
6	2000	20	1.0
6	1400	7	0.5
6	1350	0	0.0
6	1800	16	0.9

Under the conditions described above, precipitation of zirconium mandelate was effected from a solution containing a definite amount of UX_1, after which the activity of the isolated precipitate was measured.

The results of these experiments (Table 8) indicate that at low acidity (up to 1 N) UX_1 is coprecipitated with zirconium mandelate. At higher solution acidities, the amount of UX_1 trapped by the precipitate drops rapidly, and at concentrations of HCl of 1 : 1, practically all the UX_1 remains in solution.

In order to establish whether or not it is possible to purify protoactinium from radium, zirconium mandelate was precipitated from hydrochloric acid solution (HCl 1 : 1), containing $3 \cdot 10^{-8}$ g Ra. The mandelate precipitate was treated with alkali; it was then dissolved in acid and transferred to a bubbler. After a six-day accumulation of fission products, activity was measured; in all cases this did not exceed the background amounting to less than 0.03% Ra (taking into account the value of the scale division of the apparatus).

Thus, it has been established that precipitation of protoactinium with zirconium mandelate from hydrochloric acid solutions (HCl 1 : 1) allows one to establish the exact content of protoactinium.

Radiochemical purification of protoactinium is achieved in the given method by the simple operation of coprecipitating protoactinium with the crystalline precipitate of zirconium mandelate, whereas in all known methods of isolating protoactinium, the purification stage presents the main difficulty, and purification is only achieved by repeated fluoride treatments and numerous purifications from polonium.

SUMMARY

A new method has been developed for the analytical determination of protoactinium, based on coprecipitation of the latter with zirconium mandelate from hydrochloric acid solutions.

By means of this method it is possible to determine the protoactinium content rapidly, while ensuring its purification from all other natural α-active radioelements.

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PREPARATION OF SLIGHTLY SOLUBLE COMPOUNDS OF QUADRIVALENT URANIUM USING RONGALITE

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During preparation of any compound of quadrivalent uranium arising from uranyl derivatives, the first problem is reduction of hexavalent uranium to the quadrivalent state. For as complete an isolation of quadrivalent uranium as possible from solution, one can precipitate it as the slightly soluble oxalate or fluoride.

Methods have been published [1, 2], for the synthesis of the oxalate of quadrivalent uranium, in which the uranyl salts are reduced by means of hydrosulfite $Na_2S_2O_4$, or metallic copper and zinc. For his thesis, G. I. Petrazh (Mitrofanova) used reduction of the uranyl salt with hydrosulfite for preparing the oxalate of quadrivalent uranium. This method has been recommended as the most suitable way of preparing quadrivalent uranium oxalate. All the same, it must be pointed out that during reduction of acid solutions of both uranyl chloride and acetate, respectively [3], sulfur is usually formed. Presumably, sulfur is formed as the result of the following process: $2S_2O_4^{2-} + H_2O \longrightarrow S_2O_3^{2-} + 2HSO_3^-$; $S_2O_3^{2-} + 2H^+ \longrightarrow H_2O + SO_2 + S$. Bearing this in mind, it is still recommended that approximately twice the theoretical amount of hydrosulfite should be used. In order to remove the sulfur, the reduced solution must be filtered, and this process may lead to possible oxidation of quadrivalent uranium. These drawbacks led us, as long ago as 1948, to abandon this method, and two more convenient and rapid methods of preparing uranium oxalate have been devised. The first method consists of dissolving uranium metal in HCl with subsequent precipitation with oxalic acid; the second consists of the electrolytic reduction of uranyl oxalate, during which uranium oxalate is deposited on the cathode.

In 1952 we suggested another method of reducing hexavalent uranium to the quadrivalent state. Rongalite was suggested as the reducing agent; rongalite is a compound of sodium sulfoxylate and formaldehyde $NaHSO_2 \cdot CH_2O \cdot 2H_2O$.[*] It is a white crystalline material with a melting point of 63°. It is used as a reducing agent in dyeing.

A qualitative study of the interaction between rongalite and uranyl nitrate showed that rongalite reduces hexavalent uranium even at room temperature. All the same, the reaction is slow in the absence of acid. Hydrogen ions strongly accelerate the reaction, which is apparently determined by the process: $UO_2^{2+} + 2H^+ - 2e \longrightarrow UO^{2+} + H_2O$. In order to establish the optimum conditions for reduction, the requisite amounts of rongalite and HNO_3 were determined as well as the behavior of the reaction itself.

We assumed that for reduction of one gram ion of uranyl, one gram of rongalite is required:

$$UO_2^{2+} + HSO_2^- \longrightarrow UO^{2+} + HSO_3^-.$$

This assumption was checked experimentally on the basis of the ratio between amount of rongalite taken and the yield of quadrivalent uranium oxalate.

For this purpose a solution of oxalic acid (1 g of $H_2C_2O_4 \cdot 2H_2O$ in 10 ml of water) was added to 50 ml of a solution of uranyl nitrate containing 1.8 g of the hexahydrate salt and 4.4 ml of concentrated HNO_3 (d = 1.4);

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[*] On completion of this work, we learned from the published reports of the Geneva Conference ("Studies in the Fields of Geology, Chemistry, and Metallurgy" 1955 p. 31) that I. V. Moiseev reduced uranium with rongalite at 80-90°.

[**] Deceased.

this was followed by the rongalite solution (0.35 g of rongalite in 10 g water) calculated on the basis of 0.5 mole of rongalite per mole of uranium.* The precipitate of quadrivalent uranium oxalate which separated out was filtered, and then washed successively with water, alcohol, and ether; it was finally weighed. The weight of precipitate obtained proved to be 1.02 g; this amounted to about 55% of the amount of uranium oxalate (1.88 g) which could have been formed from the 1.8 g of uranyl nitrate taken. The next lot of rongalite, equivalent to a quarter mole per mole of uranium (0.17 g rongalite in 5 ml water) was then added to the filtrate. The solution was acidifed beforehand with nitric acid so that it was 1 N with respect to this acid in the final volume. The weight of uranium oxalate isolated in this stage was found to be 0.43 g (about 23%). Finally, the third lot of rongalite was added (0.17 g in 5 ml water), to the filtrate adjusted to 1 N with respect to acid, beforehand; the yield in this last stage was a further 0.36 g of uranium oxalate, equivalent to about 19%.

These experiments showed that the interaction of rongalite with uranyl salts, basically, proceeds in accordance with the equation given above.

As indicated already, hydrogen ions strongly accelerate the reaction. Actually, on addition of rongalite to a neutral solution at room temperature, the solution acquires a reddish-brown color, which slowly gets stronger, and gradually turns green, and smells strongly of sulfur dioxide and hydrogen sulfide. In 0.5 N HNO_3 solutions, the reddish-brown solution turns green within 5-10 minutes and complete reduction is achieved after 2.5 hours. On increasing the acidity to 1 N with respect to HNO_3, the time of complete reduction is cut down to 1 hour 45 minutes. With increasing acidity, the odor of H_2S gets weaker, and in 1 N HNO_3 solutions, its odor is practically undetectable.

As a result of these experiments we concluded that uranium can be satisfactorily isolated as quadrivalent uranium oxalate by the following method.

To a solution of uranyl nitrate, containing not more than 70 g of $UO_2(NO_3)_2 \cdot 6H_2O$ per liter, is added, in the cold, first, HNO_3 such that its final concentration in solution will be 1 N; oxalic acid solution is next added in an amount corresponding to a 10% excess of that required by theory; finally rongalite solution is added in an amount exceeding the theoretical amount (1 mole of rongalite per mole uranium) by 7-10%.

When this is done a grey-green, finely crystalline material separates out, which in composition is apparently a mixture of the normal and acid oxalates of uranium.** After removal of the precipitate, a qualitative reaction with $K_4[Fe(CN)_6]$ (after preliminary oxidation of uranium with nitric acid and its subsequent removal by evaporation) did not detect uranium.

The amount of uranium which can remain in solution corresponds to the solubility of quadrivalent uranium oxalate under the experimental conditions. We did not actually determine this amount, but we can get an estimate of it on the basis of some experiments and published results.

The solubility of $U(C_2O_4)_2 \cdot 6H_2O$ in 1 N HNO_3 is equal to 9.7×10^{-2} g/liter. In the presence of excess oxalic acid, this value drops somewhat. In our experiments the concentration of excess oxalic acid was equal to about 0.01 M in the final volume. According to available results [4], 0.0179 M $H_2C_2O_4$ depresses the solubility of hexavalent uranium oxalate by approximately six times, in comparison with the solubility of the corresponding salt in 0.75 M HNO_3. Taking into account this same effect in the case of $U(C_2O_4) \cdot 6H_2O$, we conclude that under the influence of excess oxalic acid, the solubility will be depressed to 1.6×10^{-2} g of the hydrated salt / liter.

In addition, according to Feigl's results, the limiting concentration of uranium which can be detected by a spot test with $K_4[Fe(CN)_6]$ is equal to 1 part in 54,000 parts of water. In our case, the amount of uranium was about 0.8 part per 54,000; this is on the limit of the sensitivity of the reaction.

As indicated already, quadrivalent uranium can be quantitatively removed from solution as the fluoride. Experiments on isolation of the fluoride of quadrivalent uranium were carried out under the same conditions as those used for isolation as the oxalate. In this case, instead of oxalic acid, 48% of hydrogen fluoride was added before reduction; the amount of hydrogen fluoride used was in slight excess of theory.

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* The rongalite preparation we used contained about 82 % of rongalite; this was established iodometrically.

** This mixture may, if required, be converted into an oxalate of the composition $U(C_2O_4)_2 \cdot 6H_2O$ by boiling in a weakly acid solution (0.2 N HNO_3 or HCl); this was confirmed by analytical results.

A bright green crystalline material is deposited from solution as reduction of uranyl proceeds. After removal of the precipitate, no uranium was detected in solution. Thus, in this case also, reduction with rongalite allows one to precipitate uranium quantitatively from solution. The question of the effect of other elements on completeness of isolation of uranium will be the object of a further study.

SUMMARY

A method of reducing uranyl salts with rongalite is described in the present article.

Rongalite, in comparison with hydrosulfite, has the advantage that no sulfur is precipitated under the conditions used.

Quadrivalent uranium can be quantitatively isolated from a solution of oxalic acid or hydrogen fluoride.

Optimum concentration conditions for isolation of uranium as the oxalate have been established.

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DETERMINATION OF GERMANIUM AS GERMANOMOLYBDIC ACID AFTER ITS SEPARATION FROM CERTAIN ELEMENTS BY AN EXTRACTION METHOD

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Germanium is most frequently separated from accompanying elements by distillation as the tetrachloride $GeCl_4$ (b.p. +83.1°), with subsequent precipitation as GeS_2. Arsenic trichloride distills over together with $GeCl_4$ [1]. Pentavalent arsenic does not form a volatile chloride. Various oxidizing agents are used for converting As^{III} into As^{V} [1-4]. Distilling $GeCl_4$ takes a lot of time and is very unsuitable, particularly for separating small amounts of germanium (the most frequent case one comes across in practical analysis). Other methods for separating germanium from arsenic (reduction of arsenic with metallic copper, precipitation of As_2S_3 in the presence of excess HF, etc.) are also tedious and not very convenient [5,6]. Newcombe's method of separating germanium from a series of elements [7], consists in distilling $GeCl_4$ from a hydrochloric or sulfuric acid solution, and extracting it from the distillate with carbon tetrachloride in the presence of 9-10 N HCl. $GeCl_4$ is re-extracted from the carbon tetrachloride with water and is determined photometrically in the form of a complex with oxidized hematoxylin. Schneider and Sandell [8], proposed a more convenient method of extracting $GeCl_4$ during determination of germanium in silicate rocks, which permitted preliminary distillation to be avoided. The possibility of separating germanium and arsenic by extraction with carbon tetrachloride (and also eliminating the effect a number of other elements) has been studied by Fischer and coworkers [9].

Undoubtedly, an extraction method of separating germanium has advantages over distillation: it is fairly rapid, easily carried out, and enables one to avoid the stage of isolating germanium as the sulfide, and permits final determination of germanium by any method.

In all the papers mentioned above, germanium was determined photometrically, using reagents which are not readily available (phenylfluorone, hematoxylin). Formation of germanomolybdic acid is a sensitive enough reaction for determining germanium. All the same, all those elements which form heteropoly acids, particularly silicon, interfere with the use of this reaction.

In accordance with what has been said above, we thought it would be expedient to establish whether or not it is possible to isolate germanium from a number of elements which form heteropoly acids, by extraction of $GeCl_4$ with carbon tetrachloride, and determine the germanium subsequently, as germanomolybdic acid.

First of all we studied the possibility of extracting $GeCl_4$ from pure salts by the technique proposed by Schneider and Sandell [8]; we modified the method very slightly (number of extractions, extent of washing the extracted layer, etc.).

A standard solution of germanium, containing 1.0 mg of GeO_2 / ml, was prepared by dissolving 0.2500 g of water soluble GeO_2 (chemically pure) in 250 ml of distilled water. Solutions containing 0.1 and 0.01 mg of GeO_2 / ml, were prepared by diluting the stock standard solution.

Extraction was carried out by adding 20 ml of concentrated hydrochloric acid diluted with water to 25 ml, and cooled for preventing volatilization of $GeCl_4$, to various amounts of standard GeO_2 solution contained in a separating funnel; 10 ml of carbon tetrachloride was then added and the whole shaken for 2 minutes. Depending on the amount of GeO_2, extraction was repeated once or twice with 5 ml lots of carbon tetrachloride. For quantities of GeO_2 ranging from 0.1 to 10 mg, three extractions are recommended; for quantities of 0.001 to

0.01 mg, one extraction. Extracts were collected in another separating funnel and washed once with 5 ml of 9 N hydrochloric acid; 6 ml of water was then added and the $GeCl_4$ re-extracted from the CCl_4 by shaking for 2 minutes. For quantities of GeO_2 of 0.1 to 10.0 mg, re-extraction with water should be carried out twice; for smaller amounts, one re-extraction is enough.

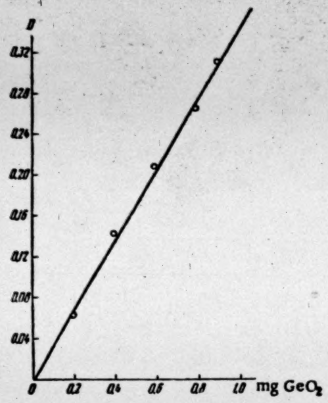

Fig. 1. Calibration curve for determining germanium as germanomolybdic acid in aqueous solutions.

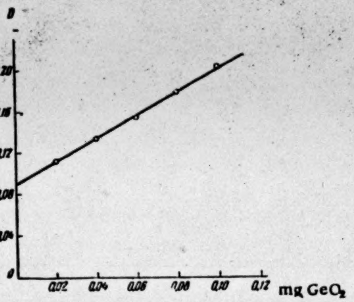

Fig. 2. Calibration curve for determining 0.001-0.014 mg germanium as germanomolybdic acid, in which isoamyl alcohol was used for extraction.

Germanium was determined photometrically as germanomolybdic acid. The aqueous solution obtained after re-extraction was transferred to a 50 ml standard flask, and 10 ml of 5% ammonium molybdate solution followed by 5 ml of 2 N sulfuric acid added; the solution was diluted with water to the mark and after 10 minutes the optical density of the yellow-colored solution was measured on a horizontal photometer at 428 mμ using a cell with layer thickness 50 mm. A calibration curve (Fig. 1) was constructed in the same way, using the standard solution of GeO_2.

TABLE 1

Determination of Germanium as Germanomolybdic Acid after Extraction of $GeCl_4$ with Carbon Tetrachloride

GeO_2 taken in mg	GeO_2 found in mg	Error in mg
0.10	0.11	+0.01
0.20	0.19	—0.01
0.30	0.28	—0.02
0.40	0.40	—0.00
0.50	0.48	—0.02
0.70	0.74	+0.04
0.80	0.85	+0.05
1.00	0.95	—0.05
2.00	1.95	—0.05
3.00	2.85	—0.15
5.00	5.00	±0.00
8.00	8.20	+0.20
10.00	9.82	—0.18

TABLE 2

Determination of Small Amounts of Germanium after Extraction with Carbon Tetrachloride

GeO_2 taken in mg	GeO_2 found in mg	Error in mg
0.0050	0.0048	—0.0002
0.0080	0.0081	+0.0001
0.0300	0.0310	+0.0010
0.0300	0.0290	—0.0010
0.0500	0.0520	+0.0020
0.0500	0.0500	±0.0000
0.0700	0.0670	—0.0030

From the results obtained which are given in Table 1, it is clear that germanium can be determined quantitatively as germanomolybdic acid after extraction of $GeCl_4$ with carbon tetrachloride. Determination of less than 0.1 mg of GeO_2 in a volume of 50 ml can be also be made with the germanium in the form of germanomolybdic acid; in this case however, it is necessary to extract with isoamyl alcohol in the presence of 1 N sulfuric acid. Pure isoamyl alcohol is used as the reference solution in this case. The results obtained are given in Table 2.

The calibration curves are shown in Figs. 2 and 3.*

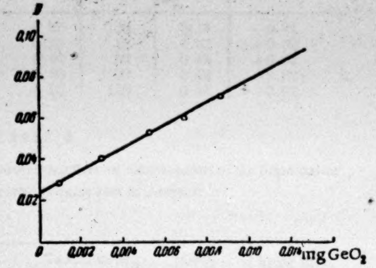

Fig. 3. Calibration curve for determination of 0.02-0.12 mg of germanium as germanomolybdic acid after extraction with isoamyl alcohol.

During a study of the extraction of $GeCl_4$ with carbon tetrachloride in the presence of various amounts of silicon, the latter was added to the germanium solution of $Na_2SiO_3 \cdot 9H_2O$, whose SiO_2 content was determined by the classical method [10], and by precipitation of silicomolybdic acid with 8-hydroxyquinoline [11].

As the results obtained show (Table 3), germanium can be quantitatively determined as germanomolybdic acid after separating it from silicon by extraction with carbon tetrachloride, as long as the ratio of $SiO_2 : GeO_2$ does not exceed 1000 : 1.

Since iron usually accompanies germanium in materials which contain the latter, we studied the effect of iron on the extractability of germanium by carbon tetrachloride. An iron solution was prepared by dissolving 16.87 g of chemically pure $FeCl_3 \cdot 6H_2O$ in 100 ml water. 1 ml of this solution contained 100 mg Fe_2O_3. Extraction of $GeCl_4$ was carried out in the presence of various amounts of iron, using the former conditions;but with the modification that the extract was repeatedly washed with 9 N Hydrochloric acid to remove iron, and only after this repeated acid washing,was water used. The results given in Table 4 were obtained for determination of germanium after separating it from iron with carbon tetrachloride.

TABLE 3

Determination of Germanium after Separating it from Silicon by Extraction of $GeCl_4$ with Carbon Tetrachloride

.Taken in mg		Ratio $GeO_2 : SiO_2$	GeO_2 found in mg	Error	
GeO_2	SiO_2			in mg	in %
0.100	0.10	1 : 1	0.120	+0.020	20
0.100	0.10	1 : 1	0.105	+0.005	5
1.000	1.00	1 : 1	1.010	+0.010	10
1.000	10.00	1 : 10	1.050	+0.050	5
0.100	1.00	1 : 10	0.096	−0.004	4
1.000	50.00	1 : 50	0.980	−0.020	2
0.010	1.00	1 : 100	0.012	+0.002	20
1.000	100.0	1 : 100	1.000	±0.000	0
0.100	100.0	1 : 1000	0.118	+0.018	18
0.100	100.0	1 : 1000	0.108	+0.008	8
0.050	100.0	1 : 2000	0.080	+0.030	60
0.030	100.0	1 : 3000	0.085	+0.055	183
0.020	100.0	1 : 5000	0.050	+0.030	150

In order to study the effect of divalent iron,a solution of 5.52 g Mohr's salt (chemically pure) in 100 ml of 2 N sulfuric acid was prepared (1 ml solution contained 12 mg FeO). Extraction of $GeCl_4$ with carbon tetrachloride in the presence of various amounts of Mohr's salt was carried out under the same conditions as those employed for extraction in the presence of ferric iron. The results obtained are given in Table 5.

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* From Figs. 1 and 2, it is clear that the intensity of the color of the solutions obeys Beer's law. The calibration curve does not pass through the origin because pure isoamyl alcohol was used as the reference solution.

TABLE 4

Determination of Germanium after Its Isolation from Ferric Iron

Taken in mg		GeO_2 found in mg	Error in mg
GeO_2	Fe_2O_3		
0.20	100	0.19	−0.01
0.30	40	0.32	+0.02
0.40	50	0.42	+0.02
0.40	70	0.42	+0.02
0.50	120	0.48	−0.02

TABLE 5

Determination of Germanium after Separation from Ferrous Iron

Taken in mg		GeO_2 found in mg	Error in mg
GeO_2	Fe_2O_3		
0,5	50	0.49	−0.01
0,5	65	0.52	+0.02
0,6	65	0.62	+0.02

TABLE 6

Determination of Germanium after Separation from Quinquevalent Arsenic

Taken in mg		GeO_2 found in mg	Error in mg
GeO_2	As_2O_3		
0.30	3	0.29	−0.01
0.40	6	0.38	−0.02
0.50	6	0.51	+0.01
0.50	9	0.49	−0.01

As the results given in Tables 4 and 5 respectively show, insignificant amounts of di- and trivalent iron do not interfere with determination of germanium as germanomolybdic acid, after separation of germanium and iron by extraction with carbon tetrachloride.

As pointed out already, separation of germanium and arsenic presents considerable difficulty. Fischer and coworkers [9], found that only trivalent arsenic is extracted with germanium from 9 N HCl; quinquevalent arsenic is not extracted; accordingly they recommend that before separation of germanium by extraction with carbon tetrachloride, trivalent arsenic should be oxidized with potassium chlorate. We checked on the influence of tri- and quinquevalent arsenic on extraction of $GeCl_4$ with carbon tetrachloride, and confirmed the conclusions of Fischer (Table 6).

Oxidation of trivalent arsenic was effected by adding a few crystals of $KClO_3$ to the solution contained in the separating funnel prior to extraction of $GeCl_4$ with carbon tetrachloride, extraction being carried out 10-15 minutes after addition of the oxidizing agent. Germanium was then determined, as in all other cases, as germanomolybdic acid.

The results given in Table 6 confirm Fischer's conclusions regarding the possibility of eliminating the effect of trivalent arsenic on determination of germanium, by oxidation of the arsenic with potassium chlorate.

SUMMARY

1. It has been confirmed that it is possible to extract $GeCl_4$ with carbon tetrachloride from solutions of pure germanium salts.

2. It has been established that it is possible to determine germanium photometrically as germanomolybdic acid after extraction.

3. A method has been developed for separating germanium from large amounts of silicon, iron, and arsenic by extraction of $GeCl_4$ with carbon tetrachloride, and subsequent determination of germanium as germanomolyb[illegible] acid.

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POTENTIOMETRIC TITRATION WITH THE FERRI-FERROCYANIDE ELECTRODE

I. DETERMINATION OF COPPER

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In the work described here we used a method described previously* for potentiometric titration of copper with potassium ferrocyanide in ammoniacal media, using a ferri-ferrocyanide electrode. The null instrument used was a self-levelling mirror galvanometer (sensitivity 200 mm/μA); the volume of solution being titrated was about 25 ml (where necessary, water was added to bring the volume up to this value); the titrant solution of $K_4Fe(CN)_6$ was more dilute (0.07500 M) and was added from a macro buret, but was prepared in the same was as before, by weighing out the requisite amount of thrice recrystallized $K_4Fe(CN)_6 \cdot 3H_2O$ which was stored over deliquescent NaBr. Standard $Cu(NO_3)_2$ was prepared from chemically pure material; its molarity as established by electrolysis was equal to 0.1762.

Ammonium hydroxide solution obtained by saturating water with dry ammonia, was stored in paraffined bottles.

TABLE 1

Cu taken in g	Concentrated NH_4OH added in ml		Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	total amount	deficit			
0.1122	1.50	0	11.05	0.1114	−0.71
0.1122	1.20	0	11.15	0.1123	+0.09
0.1122	1.10	0	11.05	0.1114	−0.71
0.1122	1.50	0	11.15	0.1123	+0.09
0.2238	1.80	0	22.15	0.2232	−0.27
0.2793	2.50	0	25.55	0.2776	−0.61
0.2793*	2.20	0.30	27.75	0.2797	+0.14
0.2793*	1.80	0.70	28.15	0.2836	+1.52

* Cupric hydroxide remained undissolved in NH_4OH.

The other reagents used were analytical grade. All solutions were made up in doubly distilled water. The empirical titer of 0.07500 M $K_4Fe(CN)_6$ in terms of copper, as determined potentiometrically according to the method described, was equal to 0.01008.

Results for titrations of solutions of pure $Cu(NO_3)_2$ are given in Table 1.

Titration results remain satisfactory, as long as the excess or deficit of NH_4OH solution, used for dissolving the cupric hydroxide, does not exceed 0.3-0.5 ml. Since the oxidation potentials of many systems are lowered on increasing pH, we titrated copper (using ammoniacal media) in the presence of KIO_3, K_2CrO_4, $NaBrO_3$, and $KClO_3$, without having to worry about oxidation of the ferrocyanide ion.

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* I. L. Teodorovich and I. K. Leushina, J. Anal. Chem. 8, 340-345 (1953).

TABLE 2

Cu taken in g	Added			Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	KIO_3 in g	conc. NH_4OH in ml				
		before precipitate dissolves	excess			
0.1122	0.15	2.20	0.90	11.15	0.1123	+0.09
0.2238	0.15	2.60	0.70	22.45	0.2262	+1.07
0.2238	0.10	2.30	0.50	22.45	0.2262	+1.07
0.2238	0.10	Before complete solution		22.25	0.2243	+0.22
0.2238	0.10		—	22.15	0.2232	—0.27
0.2793	0,15	3,70	0.90	27.85	0.2806	+0.46

TABLE 3

Cu taken in g	Added			Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	K_2CrO_4 in g	conc. NH_4OH in ml				
		before precipitate dissolves	excess			
0.1122	0.2	2.20	0.90	11.05	0.1114	—0.71
0.1122	0.2	1.30	0	11.05	0.1114	—0.71
0.2238	0.2	2.40	0.50	22.25	0.2243	+0.22
0.2793	0.2	2.90	0.10	27.65	0.2786	—0.28
0.2793	0.2	Precipitate remained	—	27.95	0.2816	+0.92

TABLE 4

Cu taken in g	Added			Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	$NaBrO_3$ in g	conc. NH_4OH in ml				
		before precipitate dissolves	excess			
0.1122	0.30	1.40	0.10	11.15	0.1123	+0.09
0.1122	0.40	1.40	0.10	11.25	0.1133	+0.98
0.1122	0.30	1.40	0.10	11.15	0.1123	+0.09
0.1122	0.30	1.40	0.10	11.15	0.1123	+0.09

Good results are obtained when ammonium hydroxide is added to the copper solution plus oxidizing agent in such amount that the precipitate does not dissolve completely, and titration is started in the presence of a small amount of precipitate. The results given in Table 2-5 also testify to the fact that in the presence of known amounts of oxidizing agent, titration of copper by this method is fully possible; this is not possible when the iodometric method is used.

TABLE 5

Cu taken in g	Added			Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	$KClO_3$ in g	conc. NH_4OH in ml				
		before precipitate dissolves	excess			
0.1122	0.3	1.40	0.10	11.05	0.1114	—0.71
0.1122	0.5	1.50	0.20	11.15	0.1123	+0.09
0.2238	0.5	1.80	0	22.15	0.2232	—0.27
0.2238	0.5	1.80	0	22.15	0.2232	—0.27
0.2793	0.5	2.50	0	27.65	0.2786	—0.28

TABLE 6

Cu taken in g	Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Titer found, T, $\frac{K_4Fe(CN)_6}{Cu}$	$Cu^{++} : Fe(CN)_6^{4-}$ in g-ions
0.1122	15.90	0.007060	1.482
0.1122	15.85	0.007081	1.485
0.2238	31.65	0.007071	1.483
0.2238	31.65	0.007071	1.483
	Mean	0.007071	1.484

TABLE 7

Cu taken in g	Added		Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	Fe^{3+} in g	conc. NH_4OH in ml			
0.1122	0.0055	1.70	11.20	0.1128	+0.53
0.1122	0,0028	1.50	11.25	0.1133	+0.98
0.1122	0,0055	1,40	11.05	0.1114	—0.71
0.1122	0.0110	1.40	11.05	0.1114	—0.71
0.1122	0,0330	1.60	11.25	0.1133	+0.98
0.2238	0.0220	2.70	22.25	0.2243	+0.22
0.2238	0.0275	2.70	22.20	0,2238	0.00

Establishment of titration conditions for copper in the presence of ammonium salts is of practical interest, since ammonium ions can prevent coprecipitation of other ions during formation of copper ferrocyanide, and also, in view of the fact that in analytical practice there is often formed a considerable amount of ammonium salts during neutralization of acid solutions.

We knew [1], that addition of ammonium nitrate to the solution being titrated leads to a considerable increase in amount of potassium ferrocyanide solution used. Nevertheless, we found out that for a content of 1.25-1.50 g of ammonium nitrate in a solution containing 0.1122 g of copper, and 2.5 g ammonium nitrate in solutions containing 0.2238 g copper, the amount of potassium ferrocyanide used remained constant (the potential jump at the end point becomes less clear cut, but still good enough). The color of the precipitate in the

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* No corresponding literature reference appears in the original — Publisher's note.

TABLE 8

Cu taken in g	Added		Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
	Sn^{++} in g	conc. NH_4OH in ml			
0.1122	0.0027	1.30	11.15	0.1123	+0.00
0.1122	0.0159	1.45	11.15	0.1123	+0.09
0.1122	0.0212	1.50	11.15	0.1123	+0.09

TABLE 9

Cu taken in g	Impurities added in g		Concentrated NH_4OH added in ml	Amount of 0.07500 M $K_4Fe(CN)_6$ solution used in ml	Cu found in g	Relative error in %
0.2238	$Bi(NO_3)_3$	0.004	2.5	31.65	0.2239	+0.04
0.1122	$SbCl_5$	0.006	1.4	15.80	0.1118	−0.36
0.1122	$SbCl_5$	0.03	2.8	16.35	0.1156	+3.03
0.1122	$KCr(SO_4)_2$	0.014	1.35	15.20	0.1075	−4.19
0.1122	$Al(NO_3)_3$	0.01	1.35	15.95	0.1128	+0.53
0.1122	$Al(NO_3)_3$	0.002	1.2	15.75	0.1114	−0.71
0.1122	$Al(NO_3)_3$	0.007	1.25	15.75	0.1114	−0.71
0.1122	$SnCl_4$	0.59	1.5	15.75	0.1114	−0.71
0.2238	$SnCl_4$	0.59	2.6	31.65	0.2239	+0.04
0.1122	$FeNH_4(SO_4)_2$	0.13	1.5	16.00	0.1132	+0.89
0.1122	$FeNH_4(SO_4)_2$	0.16	1.6	16.20	0.1146	+2,14
0.2238	$Pb(NO_3)_2$	0.1	2.6	31.60	0.2235	−0,13

presence of NH_4NO_3 becomes red-brown whereas, under normal conditions, it was greenish-yellow. This seems to indicate formation of the double salt copper-ammonium ferrocyanide* and necessitates correcting our earlier expressed view [1].**

Titration results are given in Table 6.

We also titrated copper in the presence of a number of other cations (in solutions free from ammonium nitrate and also in solutions containing the latter). Ammonium hydroxide was added before titration until the blue precipitate of cupric hydroxide had dissolved, as observed visually.

Results of these determinations are given in Tables 7, 8, and 9. In a number of cases it seems that the presence of NH_4^+ ions prevents coprecipitation to an appreciable extent.

It should be noted that titration of solutions of $ZnSO_4$ and also of total $ZnSO_4$ and $Cu(NO_3)_2$ gives reproducible results.

SUMMARY

Copper has been potentiometrically titrated with potassium ferrocyanide. It has been demonstrated that it is possible to titrate copper by the given method in the presence of the oxidizing agents KIO_3, K_2CrO_4, $NaBrO_3$, and $KClO_3$, and in the presence of certain cations.

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* It is possible that potassium ions may get into the precipitate as well.

** See footnote on preceding page – Publisher's note.

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EXTENT OF REDUCTION OF THE NITRATE ION ON A DROPPING MERCURY CATHODE

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Recently some success has been achieved in studying the mechanism of the reduction of the nitrate ion on a dropping mercury cathode. The effect of the valence of indifferent electrolyte cations on the kinetics of the reduction of the anions has been given a simple explanation from the point of view of the theory of delayed discharge [1]. An explanation has been given of the mechanism of the origin of current jumps and hysteresis loops during reduction of the nitrate ion in weakly acid and neutral solutions of lanthanum chloride [2]. Explanations have also been given for phenomena observed during reduction of the nitrate ion in more acid solutions of $LaCl_3$ [3,4]. All the same, some questions related to reduction of the nitrate ion on a dropping mercury cathode still remain open, or disputable. Discussion regarding the extent of reduction of NO_3^- ions, for example, continues. As will become evident, there are very diverse opinions on this question; knowledge of the extent of reduction of NO_3^- ions at the same time is of considerable interest. In this connection therefore, in the present article we have tried to make a critical evaluation of available experimental data, and the conclusions based on this data, regarding the products of reduction of the nitrate ion in the presence of uni-, di-, or trivalent cations. We shall turn to the question of the extent of reduction of NO_3^- ions in the presence of cations of higher valence in a future article.

In the early work of electrochemists of Ya. Heyrovský's school, which was devoted to studies of the reduction of nitrate ions on a dropping mercury cathode [5,6], it was confirmed that in the presence of lanthanum salts, the NO_3^- ion is reduced to ammonia:

$$NO_3^- + 8e^- \longrightarrow NH_3. \qquad (1)$$

This result was obtained by comparing the wave height for reduction of Cd^{2+} and NO_3^- ions when these ions were simultaneously present in solution as $Cd(NO_3)_2$. All the same it was soon shown [7], that the reduction waves of cations which hydrolyze readily, and oxygen-containing anions, respectively, are not additive. Thus, if the concentration of Zn^{2+} ions in a solution of $LaCl_3$ containing $Zn(NO_3)_2$, is increased, while the concentration of NO_3^- ions is left unchanged, then, despite the increase in wave height for zinc, the total wave height for Zn^{2+} and NO_3^- remains unchanged until the height of the Zn^{2+} wave becomes equal to that of the NO_3^-. On increasing Zn^{2+} concentration further, the Zn^{2+} wave continues to increase. It was shown later [3, 4, 8, 9], that the reason for this nonadditivity of wave heights is the formation of hydroxyl ions as a result of reduction of NO_3^- ions,

$$NO_3^- + 8e^- + 10H^+ \longrightarrow NH_4^+ + 3H_2O \text{ (in acid media);} \qquad (2)$$

$$NO_3^- + 8e^- + 7H_2O \longrightarrow NH_4^+ + 10\,OH^- \text{ (in neutral media);} \qquad (3)$$

leading to a drop in the charge of the cations, or even to precipitation of hydroxides or basic salts. On these grounds, the reduction waves for H^+ and NO_3^- ions should also be nonadditive. As experiment has shown, in the presence of lanthanum salts, for a not too high acid concentration, H^+ ions are discharged at more negative potentials than NO_3^- ions (Fig. 1). As a consequence, the wave for discharge of H^+ ions when solutions of $LaCl_3$ containing KNO_3 are acidified, in general does not appear until the flow of H^+ ions to the cathode becomes equal to the flow of OH^- ions, which originate during reduction of NO_3^-, in the opposite direction. Consequently, a comparison of wave heights for reduction of cations and NO_3^- ions, respectively, when both are present simultaneously in solution, with the idea of establishing the extent of reduction of NO_3^- ions, cannot lead to satisfactory results. With this aim in view one could compare wave heights measured separately. Nevertheless, when this is done, no account is taken of differences in diffusion coefficients of NO_3^- ions and test cation. Neglect of these differences in diffusion coefficients during comparisons of wave heights can distort the results essentially. Accordingly, the statement referred to above concerning reduction of nitrate ion to ammonia in the presence of $LaCl_3$, requires additional checking. The method under discussion has also been used by other investigators. Thus, S. L. Sinyakova and G. G. Karanovich [10] found that in the presence of lanthanum and neodymium salts, nitrate ions are reduced into equimolar amounts of a mixture of hydroxylamine and ammonia, i.e., with the expenditure of seven electrons for one ion of NO_3^-. In the presence of $CeCl_3$, the number of electrons, determined by the same method, proved to be five, whereas substitution of lanthanum or neodymium salts by a cerium salt, should, in principle, introduce no new effect.

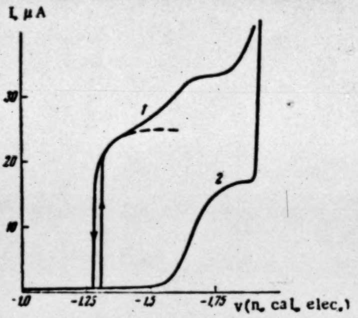

Fig. 1. Polarographic waves for NO_3^- and H^+ in the presence of $LaCl_3$. 1) 0.1 M $LaCl_3$ + 10^{-3} M KNO_3 (pH ~6.6); 2) 0.1 M $LaCl_3$ + $1.94 \cdot 10^{-3}$ M HCl; a hysteresis loop is shown on Curve 1.

The number of electrons n used for reduction of one ion of NO_3^- can be calculated by means of the Ilkovich equation:

$$i_d = 605nD^{1/2} cm^{2/3} \tau^{1/6}, \qquad (4)$$

where i_d is the limiting current, D is diffusion coefficient, c is the concentration of depolarizer, m the outflow rate, and τ the dropping time of mercury from the capillary. In this way, Kolthoff, Harris, and Matsujama [11], calculated n for reduction of NO_3^- ions in the presence of $LaCl_3$, and found that it was equal to six, which corresponds to reduction of nitrate ions to hydroxylamine. The value of the diffusion coefficient used for this calculation, was calculated from the results on equivalent electrical conductivity at infinite dilution λ_0 by means of Nernst's equation

$$D_0 = \frac{RT}{ZF} \lambda, \qquad (5)$$

where Z is the valence of the ion. It is known however, that diffusion coefficients depend to a considerable degree on the concentration and nature of the indifferent electrolyte. Consequently, the use of values for diffusion coefficients, calculated on the basis of Nernst's equation, for determining n by means of the Ilkovich equation, cannot be regarded as justified, particularly for large values of n, as in the case of NO_3^- reduction. Results for real diffusion coefficients, i.e., ionic diffusion coefficients in solutions containing a large amount of indifferent electrolyte, are nonexistent in the case of NO_3^- ions. On the other hand, Ilkovich's equation as well as other, more accurate, equations, have come into use for calculating real diffusion coefficients from experimental data on the values of limiting currents for known values of n [12-15].

Methods involving direct experimental determination of the value of n based on the laws of electrolysis, viz. conductometric [16], and micro-conductometric [17, 18], methods, are more reliable. Grabowscki [19], carried out a micro-conductometric determination of n for reduction of NO_3^- in the presence of $LaCl_3$. According to his results, in the presence of $LaCl_3$, the nitrate ions are reduced to an equimolar mixture of hydroxylamine and ammonia, since n proved to be equal to 6.8 (about 7). The solution left after hydrolysis gave a positive reaction for ammonia (Nessler's reagent) and for hydroxylamine (decolorization of $KMnO_4$ solution).* In this connection, Grabowscki is of the opinion that ammonia accumulates in solution as the result of further reduction of hydroxylamine, which, according to him, is only partial in alkali solutions. This last opinion is not confirmed by our results [20,21], according to which, in the presence of lanthanum salts, the extent of reduction of hydroxylamine does not depend on pH, for all those values at which hydroxylamine is reduced. When considering the results of micro-conductometric determination, the following circumstances should be borne in mind.

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* It should be pointed out that decolorization of $KMnO_4$ solution in the given instance cannot serve as a qualitative reaction for hydroxylamine, since this decolorization could be brought about by other reduction products, such as nitrite.

While the amount of hydroxyl ions which develop on reduction of nitrate ions on a dropping mercury cathode is not enough to lead to an appreciable change in the composition of the large volume of solution, which one normally deals with in polarography, on prolonged electrolysis of small volumes of solution, as is the case during micro-conductometric determination, one should expect an essential change in the composition of the solution. In solutions containing $LaCl_3$ there is danger of precipitation of hydroxides or basic salts of lanthanum; in the latter event, the concentration of nitrate ion will decrease. Further, as has been shown earlier [2], for insufficiently strong alkalization of the $LaCl_3$ solution, the reduction wave for NO_3^- ions is strongly distorted a long time before quantitative precipitation of lanthanum hydroxide, which should, presumably, depress n. A low value for n can also be obtained as the result of insufficient agitation of the solution, such as was the case, e.g., in Grabowscki's experiment, where the solution was agitated by the falling drops of mercury. As a result of this the current flowing into the dropping mercury electrode may drop during the electrolysis process more rapidly than accords with the decrease in NO_3^- concentration throughout the body of the solution. On the basis of these considerations, it seems likely that the results obtained by Grabcwscki may be rather lower than the true values of n. Meites [22], has also used the microcoulomb-metric method for determining n in the case of reduction of NO_3^-. On the basis of his results, Meites came to the conclusion that in LiCl and $CeCl_3$ solutions, the nitrate ion is not reduced, and that the wave which is observed in these solutions corresponds to the catalytic reduction of hydrogen ions. This result contradicts all experimental data accumulated hitherto and obviously does not correspond to fact.

Collat and Lingane [23] tried to carry out a coulomb-metric determination of NO_3^- ion reduction. With this aim in view they subjected to prolonged electrolysis at constant potential (-1.4 v with respect to the saturated calomel electrode in the presence of $LaCl_3$, and -1.7 v in the presence of $CeCl_3$) on a large mercury cathode, solutions of $LaCl_3$ and $CeCl_3$ containing low concentrations of KNO_3 (of the order of 10^{-3} M/liter); they carried on electrolysis until practically all NO_3^- ions had been reduced. After analysis, the solution was quantitatively analyzed for nitrate, nitrite, hydroxylamine, hydrazine, ammonia, and acid. The pH of the solution was controlled continuously by means of a glass electrode and maintained constant (5-7) by periodic addition (when necessary) of standard hydrochloric acid solution. As experiment showed, the main products of reduction of NO_3^- in the presence of $LaCl_3$ and $CeCl_3$ are hydroxylamine and ammonia ($n = 7$). The authors point out that it is possible for small amounts of gaseous products to be formed (nitrogen and nitric oxide). Nitrite and hydrazine were not detected. When one gets thoroughly acquainted with these results, it becomes doubtful whether the extent of reduction of NO_3^- ions at -1.4 and -1.7 v, as follows from the work of Collat and Lingane, was the same. It is known that in weakly acid and neutral solutions of lanthanum chloride, the nitrate ion gives two polarographic waves (See Fig. 1, Curve 1). It is obvious that these waves correspond to two different degrees of reduction of the NO_3^- ion. As can be seen from Fig. 1, the limiting current of the first wave corresponds to -1.4 v, while the limiting current of the second wave occurs at -1.7v. Accordingly, the results of the coulomb-metric measurements at these potentials should be equal.

In order to determine the number of electrons n, which are expended on the reduction of one ion of NO_3^-, one can proceed as follows. It has been pointed out above that it is possible, by using Ilkovich's equations, to calculate real diffusion coefficients from the value of the limiting current for a known value of n.

Let us calculated, e.g., the diffusion coefficient of hydrogen ions in the presence of 0.1 M $LaCl_3$, and compare it with the value of the diffusion coefficient of the H^+ ion at infinite dilution as calculated by means of Nernst's equation (9.34×10^{-5} cm^2/sec [24]).

In Fig. 2 are shown polarization curves of 0.1 M $LaCl_3$ solutions containing different amounts of hydrochloric acid.* In order to determine the limiting current with respect to hydrogen, the curves have to be extrapolated to a potential region which is somewhat more negative than the discharge potential of the supporting electrolyte cations. In Fig. 2, the extrapolation is depicted by the dashed portions. A graph for the relation between the limiting current for hydrogen ion discharge and acid concentrations, constructed on the basis of the results given in Fig. 2, is given in Fig. 3. At HCl concentration of 5×10^{-3} N, the limiting current with respect to hydrogen ions is equal to 46 μA.

Obviously, the Ilkovich equation can only be used in the case where the wave is not distorted by polarographic maxima. Maxima of the second kind, can, as is well known, be almost entirely eliminated by using

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* Results on the effect of pH on the kinetics of reduction of La^{3+} ions (compare curves 1-4 on Fig. 2) have been published and explained previously [21].

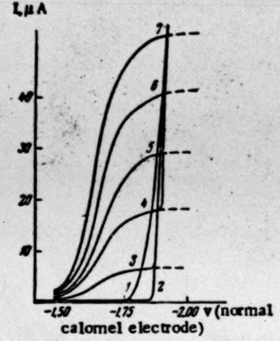

Fig. 2. Polarization curves for solutions of: 1) 0.1 M $LaCl_3$ (pH ~ 7.5); 2) 0.1 M $LaCl_3$ (pH ~ 6); 3) 0.1 M $LaCl_3$ + $0.663 \cdot 10^{-3}$ M HCl; 4) 0.1 M $LaCl_3$ + $1.96 \cdot 10^{-3}$ M HCl; 5) 0.1 M $LaCl_3$ + + $3.23 \cdot 10^{-3}$ M HCl; 6) 0.1 M $LaCl_3$ + $4.46 \cdot$ $\cdot 10^{-3}$ M HCl; 7) 0.1 M $LaCl_3$ + $5.65 \cdot 10^{-3}$ M HCl.

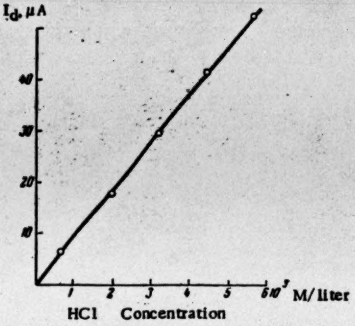

Fig. 3. Relation between limiting current of H^+ ion discharge and hydrochloric acid concentration (indifferent electrolyte 0.1 M $LaCl_3$).

not very concentrated solutions, and low discharge rates of mercury from the capillary. These conditions were fulfilled in our experiments. All the same, in order to be absolutely sure that no maxima are present, we studied the effect of additions of gelatin on the discharge wave of H^+ in the presence of 0.1 M $LaCl_3$. These results are given on Fig. 4.: they show that additions of gelatin in sufficient amount to suppress maxima, lead to a shift of the H^+ wave to positive values, i.e., they facilitate discharge of H^+ ions,* without lowering the height of the wave (Fig. 4. Curves 2-4). Consequently, under these conditions, the discharge wave of H^+ ions is not distorted by maxima.** Depression of the wave height for hydrogen ion discharge, on addition of large amounts of gelatin (Fig. 4, Curve 5-6), cannot be ascribed to suppression of maxima, but is caused by other factors, e.g., by an increase in viscosity of the solution, by blocking of the drop surface by adsorbed gelatin, or by both simultaneously.

The flow rate of the mercury and the dropping period necessary for further calculations were determined in 0.1 M $LaCl_3$ at -1.7 v; they are respectively equal to 1.81 mg/second and 3.8 seconds. From the Ilkovich equation (4), we have:

$$D_{H^+} = \left(\frac{i_d}{605 \cdot n \cdot c \cdot m^{2/3} \tau^{1/6}}\right)^2 = \left(\frac{46}{605 \cdot 1 \cdot 5 \cdot 1.81^{2/3} \cdot 3.8^{1/6}}\right)^2 = 6.73 \cdot 10^{-5} \text{ cm}^2/\text{sec}.$$

Let us assume that the diffusion coefficients of H^+ and NO_3^- ions in 0.1 M $LaCl_3$ are reduced in value, in comparison with the diffusion coefficients of these ions in an infinitely dilute solution, to an equal extent, i.e., that:

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* According to published results [25], depression of hydrogen over-voltage under the effect of additions of gelatin have also been observed in the presence of KCl. Apparently, the indicated lowering of hydrogen over-voltage by gelatine which contains amines, is explained by the possibility of the development of a new mechanism for hydrogen ion discharge: $BH^+ + e^- \rightarrow B + H_{agc}$; $B + H^+ \rightarrow BH^+$, where B is the molecule of a weak base [26].

** In the presence of gelatin, the wave for H^+ discharge has a distinct limiting current. Curves 2 and 4, among others, demonstrate the correctness of the method of extrapolating we have used for determining I_d.

$$D_{NO_3^-} = 1.92 \cdot 10^{-5} \frac{6.73 \cdot 10^{-5}}{9.34 \cdot 10^{-5}} = 1.38 \cdot 10^{-5} \quad \text{cm}^2/\text{sec}.$$

This assumption has still not had direct experimental confirmation. All the same, the result obtained on the basis of this assumption is of interest since it is also confirmed by other results.

Let us calculate the number of electrons participating in the reduction of one ion of NO_3^-. According to the results of numerous measurements at a concentration of 10^{-3} M/liter of NO_3^- and at $m = 1.81$ mg/second, and $\tau = 3.8$ seconds (at -1.7 v) the limiting current for reduction of NO_3^- in 0.1 M $LaCl_3$ is equal to 32 μA. Substituting these values in the Ilkovich equation, we get:

$$n = \frac{i_d}{605 \cdot c \cdot D^{1/2} m^{2/3} \tau^{1/6}} = \frac{32}{605 \cdot 1 \cdot (1.38 \cdot 10^{-5})^{1/2} 1.81^{2/3} 3.8^{1/6}} = 7.8.$$

The value of n is nearly eight which indicates reduction of NO_3^- ions to ammonia. Mention has been made already of experimental data of other investigators who succeeded qualitatively in proving the formation of ammonia as the result of electrochemical reduction of nitrate ions [19,23]. We may add further that ammonia has also been detected after prolonged electrolysis of nitric acid solutions of niobium [27]. On this basis, the authors concluded correctly, that in this case the polarographic wave corresponds to reduction of nitrate ion and not of niobium. In one of a number of previous communications [20], results were given concerning simultaneous reduction of NO_3^- ions and hydroxylamine, which testify that the end product of the reduction of NO_3^- ions in 0.1 M $LaCl_3$ is ammonia. All these facts taken together, presumably, leave one in no doubt as to the correctness of this conclusion.

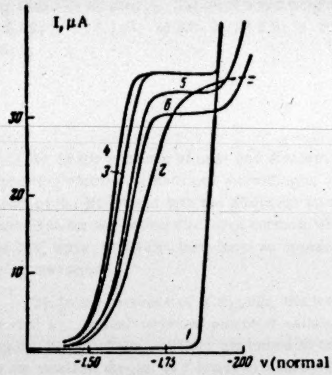

Fig. 4. Effect of additions of gelatin on discharge wave of H^+ ions. Composition of the solutions: 1) 0.1 M $LaCl_3$; 2) 0.1 M $LaCl_3$ + $4 \cdot 10^{-3}$ M HCl; 3) 0.1 M $LaCl_3$ + $4 \cdot 10^{-3}$ M HCl + $3.2 \cdot 10^{-3}$ % gelatin ; 4) 0.1 M $LaCl_3$ + $4 \cdot 10^{-3}$ M HCl + + $9.5 \cdot 10^{-3}$ % gelatin ; 5) 0.1 M $LaCl_3$ + $4 \cdot 10^{-3}$ M HCl + $6.30 \cdot 10^{-2}$ % gelatin ; 6) 0.1 M $LaCl_3$ + + $4 \cdot 10^{-3}$ M HCl + 0.111 % gelatin .

It is possible to show that in 0.1 M $LaCl_3$, the nitrite ion, at sufficiently negative potentials, is also reduced to ammonia. For this purpose, it is sufficient to compare wave heights for reduction of NO_3^- and NO_2^- ions respectively, at equal concentrations (Fig. 1, Curve 1, Fig. 5, Curve 3). Two waves are observed for reduction of NO_2^- as for NO_3^- reduction (Fig. 5). The total heights for the sum of the two waves for NO_3^- and NO_2^- respectively, corrected for residual current, are respectively 32 and 25 μA. When one takes into account that the diffusion coefficients of NO_3^- and NO_2^- ions, respectively, are practically the same, then for reduction of NO_2^- n = 6, which corresponds to reduction to ammonia:

$$NO_2^- + 6e^- + 8H^+ \longrightarrow NH_4^+ + 2H_2O. \qquad (6)$$

It has been pointed out that two waves are obtained in each case for reduction of NO_3^- and NO_2^- ions, respectively. In one of our previous papers [20], we suggested, and also brought forward some proof, that the first of these two waves corresponds to reduction of nitrate or nitrite to hydroxylamine, while the second wave corresponds to reduction of hydroxylamine to ammonia. In accordance with this assumption, the

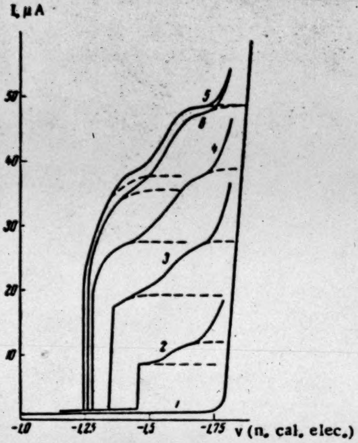

Fig. 5. Polarographic waves for reduction of NO$_2^-$ ions in the presence of 0.1 M LaCl$_3$. Composition of the solutions: 1) 0.1 M LaCl$_3$; 2) 0.1 M LaC + l$_3$ $5 \cdot 10^{-4}$ M NaNO$_2$; 3) 0.1 M LaCl$_3$ + $0.99 \cdot 10^{-3}$ M NaNO$_2$; 4) 0.1 M LaCl$_3$ + $1.48 \cdot 10^{-3}$ M NaNO$_2$; 5) 0.1 M LaCl$_3$ + $1.96 \cdot 10^{-3}$ M NaNO$_2$; 6) gelatin was added to solution 5. Ratios of wave heights: 2) 2.06 : 1; 3) 2.1 : 1; 4) 2.2 : 1; 5) 3.2 : 1; 6) 2.6 : 1.

wave heights for NO$_3^-$ and NO$_2^-$ should be in the ratio of 6 : 2 and 4 : 2 to each other, respectively. Unfortunately, in order to determine the wave heights of NO$_3^-$ and NO$_2^-$, it is necessary to resort to extrapolation, which inevitably means a loss of accuracy. Nevertheless, we established fairly definitely that the wave heights for NO$_3^-$ actually follow the ratio 24 : 8 or 6 : 2 (See Fig. 1). In the case of NO$_2^-$, the ratio of the wave heights is near to 4 : 2 at very low concentrations of NO$_2^-$ (Fig. 5. Curves 2–4), but differs appreciably from this ratio at higher NO$_2^-$ concentrations (Fig. 5. Curve 5). We suggested that in the latter case, the NO$_2^-$ wave is distorted by maxima. In order to prove this assumption, a small lump of gelatin was added to the solution, and the polarographic curve taken again after bubbling hydrogen through the solution (Fig. 5. Curve 6). In fact, after addition of gelatin, the ratio of the wave heights became closer to the value of 4 : 2. Consequently, the first wave for NO$_2^-$ also corresponds to reduction to hydroxylamine, while the second corresponds to reduction of hydroxylamine to ammonia.

The question of the relation between extent of reduction of NO$_3^-$ ions and the valence of the cation of the indifferent electrolyte is not completely clear. The opinion has been advanced that the extent of reduction of NO$_3^-$ depends considerably on the valence of the supporting electrolyte cation. Thus, according to Tokuoka and Ruzicka [6], the wave height for reduction of NO$_3^-$ is higher, the higher the valence of the cation. The results which we obtained are in agreement with this hypothesis (Fig. 6). All the same, before drawing any conclusions about the relation between extent of reduction of NO$_3^-$ and cation valence, it is necessary to take into account some other factors which also affect wave height.

1) In the presence of uni- and divalent cations, the NO$_3^-$ wave is strongly distorted by the discharge of supporting electrolyte cations. Accordingly, instead of getting a clear cut polarographic wave we get a smooth fusion of the NO$_3^-$ wave into the discharge wave for supporting electrolyte cations (Fig. 6. Curves 4 and 6). The correction for the cation discharge current, which must be introduced in order to determine the true height of the NO$_3^-$ wave, probably, introduces an appreciable error, since the correction is of the same order as the value being measured.

2) In the presence of (CH$_3$)$_4$NBr, the wave is shifted to the region of very negative potentials (from -2.0 to -2.5 v). At such negative potential values, additional difficulties connected with a breakdown in the operating conditions of the capillary are bound to crop up. The dropping mercury electrode becomes very sensitive to the smallest shocks, as a result of which the mercury ceases to drop regularly. Moreover, electrolyte penetrates into the capillary leading to periodic breaking of the circuit. As a result, the current registered is lower than that which is observed under normal capillary operating conditions.

3) On comparing the wave heights of NO$_3^-$ in different solutions (Fig. 6. Curves 2, 4, and 6) it is essential to take into account corrections for changes in dropping period, and mercury flow rate with change in potential. When the potential changes, the surface tension on the mercury – solution boundary changes. The magnitude of the surface tension determines the dropping period directly, while changes in the value of the surface tension have only a small effect, via changes in the value of the counter-pressure, on the flow rate of the mercury. Since the value of the counter-pressure usually does not exceed 3-5% of the length of the mercury column

(See [24], p. 80), then changes in mercury flow rate with electrode potential change can be neglected without appreciable error. Taking into account the correction for changes in dropping period with potential (τ = 3.8 seconds at -1.7 v, 2.5 seconds at -2.1 v, and about 1 second at -2.5 v) leads to an increase in the limiting current for reduction of NO_3^- in $CaCl_2$ solution from 25.5 μA to 28 μA. This last value already differs appreciably from the value of the limiting current for NO_3^- in a supporting electrolyte of 0.1 M $LaCl_3$ (32 μA). It should be remembered that when comparing wave heights for NO_3^- in the presence of 0.1 M $LaCl_3$ and 0.5 M $CaCl_2$ respectively, we did not take into account differences in the diffusion coefficient of NO_3^- in these solutions. It is possible that in 0.5 M $CaCl_2$, the ionic strength of which is 2.5 times that of 0.1 M $LaCl_3$, the diffusion coefficient of the NO_3^- ion is somewhat less than in 0.1 M $LaCl_3$. Accordingly we suggested that the nitrate ion is reduced to ammonia in both $LaCl_3$ and $CaCl_2$. In order to prove this assumption we tried to detect ammonia qualitatively after prolonged electrolysis at -2.0 v of a solution of $CaCl_2$ containing NO_3^-. In fact, Nessler's reagent gave a positive result for presence of ammonia in this solution.

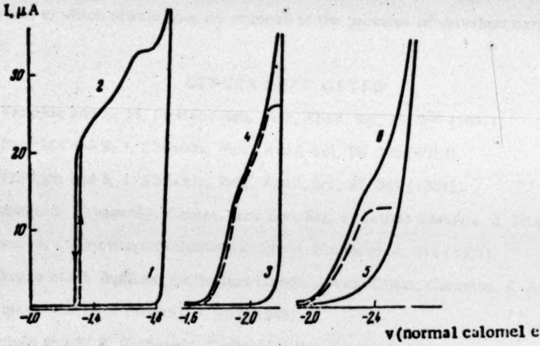

Fig. 6. Effect of the valence of supporting electrolyte cations on the shape of the NO_3 wave. 1) 0.1 M $LaCl_3$; 2) 0.1 M $LaCl_3$ + 10^{-3} M KNO_3; 3) 0.5 M $CaCl_2$; 4) 0.5 M $CaCl_2$ + 10^{-3} M KNO_3; 5) 0.5 M $(CH_3)_4NBr$; 6) 0.5 M $(CH_3)_4NBr$ + 10^{-3} M $(CH_3)_4NNO_3$ (NO_3^- waves corrected for supporting electrolyte current are shown by dotted lines).

A correction for change in dropping period with potential, increases the limiting current for NO_3^- reduction in the presence of 0.5 M $(CH_3)_4NBr$ from 12.5 μA (Fig. 6, Curve 6) to 15.6 μA. The latter value is approximately half the limiting current for NO_3^- at the same concentration in a supporting electrolyte of 0.1 M $LaCl_3$. It is possible that such a low value for the limiting current of NO_3^- in a supporting electrolyte of $(CH_3)_4NBr$ is determined by the reasons put forward already under points 1 and 2 above. Equally probable is the assumption that in the presence of $(CH_3)_4NBr$ reduction of nitrate does not go all the way to ammonia, but only to some intermediate product. In this connection the results of Collat and Lingane on coulomb-metric measurements of acid solutions of KCl, containing KNO_3 [23], are of interest. In this solution Collat and Lingane detected a maximum on the wave for H^+ ion discharge. Kemula and Grabowsky [4], (see also [3]) first gave a correct explanation for the mechanism of the development of such maxima. On reaching the reduction potential of the NO_3^- ions, the limiting current for H^+ ions should decrease and approach the limiting current for NO_3^-, on account of the excess of hydrogen ions used up over that of the electrons used during reduction of NO_3^- [see equations (2) and (3)]. Collat and Lingane postulated that the minimum of the current corresponds to the limiting current with respect to NO_3^-. As a result they conducted the electrolysis at the potential corresponding to the minimum of the current, i.e., at -1.87 v with respect to the saturated calomel electrode, or -1.9 v with respect to the normal calomel electrode. Analysis of the solution after electrolysis showed that about 68% of the nitrate had been reduced to nitrite under these conditions. From the results given in Fig. 6 (Curve 6), it follows however, that at -1.9 v in the presence of $(CH_3)_4NBr$ reduction of NO_3^- only starts to proceed at an appreciable velocity. It is possible that in the presence of KCl reduction of NO_3^- starts somewhat earlier than in the presence of $(CH_3)_4NBr$. The probability that at -1.9 v the limiting current of NO_3^- is attained in the presence of KCl is, however, low. It must be emphasized that a current minimum on the hydrogen ion discharge wave cannot be used as an indication that one is getting a limiting current with respect to NO_3^-, since its true position on the potential axis cannot be determined on account of the superposition of the discharge of supporting electrolyte cations.

SUMMARY

1. It has been shown that in the presence of $LaCl_3$ nitrate and nitrite ions are reduced to hydroxylamine at the potentials of the first wave (to -1.5 v), while at more negative potentials they are reduced to ammonia.

2. At sufficiently negative potentials the nitrate anion is reduced to ammonia in the presence of $CaCl_2$ also.

3. The extent to which nitrate ions are reduced in the presence of univalent cations cannot be regarded as settled.

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METHODS FOR THE ISOTOPIC ANALYSIS OF WATER

2. NEW LIQUIDS FOR THE DROP METHOD OF ISOTOPIC ANALYSIS OF WATER WITH A DEUTERIUM CONCENTRATION UP TO 100 AT. %

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In a previous article [1], we described a drop method for measuring the density of water. The use of mixtures of chlorobenzene and xylene for isotopic analysis of water with a deuterium content greater than 6 at. % is not very convenient in practice, since the composition of such mixtures changes comparatively easily (as a result of the appreciable and different vapor pressures of the components) and no suitable standards are available for checking it. Accordingly, in order to determine the dropping time, it is desirable to use individual materials or mixtures of materials with near and low values of the vapor pressures.

In the work described here we used diphenylmethane and mixtures of diphenylmethane and α-chloronaphthalene. The boiling points of these materials are 264.5 and 259.3° at 760 mm. The melting point of diphenylmethane is 26.5°, consequently dropping time must be measured at 30°.

The materials used were "pure" grade reagents supplied by the Kharkov reagent factory which were vacuum distilled. The density of diphenylmethane at various temperatures can be expressed by the equation: $d_4^t = 0.99822 - 0.00075\,(t-30)$, while for α-chloronaphthalene the corresponding equation is $d_4^t = 1.18495 - 0.00080\,(t-30)$. The viscosity (in centipoises) of the latter at various temperatures is 28°: 2.59 and 2.81; 30°: 2.47 and 2.68; 32°: 2.33 and 2.53. At 34 and 36° the viscosity of diphenylmethane is 2.35 and 2.14, respectively.

Using diphenylmethane it is possible to analyze water containing from 6 to 27 at. % D.* In the range 6-18 at. % accuracy of measurement is 0.1 at. %, while in the range 18-27 at. % the accuracy is about 0.25 at. %. The relative error varies from 0.5 to 1.3% depending on the range of the calibration curve in view of its hyperbolic character.

In the course of the work the solubility of diphenylmethane in water was checked. Diphenylmethane was saturated with water (98 at. % D) at 30° in the course of several hours. After removal of water by centrifuging (at the same temperature) an aliquot of diphenylmethane was ignited and the concentration of D in the water from the combustion determined. It was found that about 0.03 % of water dissolves in diphenylmethane. In order to get reproducible results for measurements of dropping time, the diphenylmethane must be treated beforehand with water (10-15 at. % D) as indicated above. A check on the calibration curve 5 years after it was constructed showed it to be completely reproducible.

The use of mixtures of diphenylmethane and α-chloronaphthalene which permits one to analyze water containing from 20 to 100 % D, requires 10 and more calibration curves according to the accuracy required. The relative accuracy of a measurement on an average amounts to 0.5%. The accuracy of measurements in the range 18-27 % D, when the mixtures described above are used, is greater than when diphenylmethane alone is used.

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* At 34°, diphenylmethane can be used for isotopic analysis of water with concentrations of 5-25 at. % D.

The dropping time in a test tube for water containing the lowest concentration of D for the range studied, when the above mixture is used, should amount to 100-120 seconds: this corresponds to a density difference between falling drop and mixture of the order of 0.005 units of density. For mixtures whose densities cover the range from 1.01 to 1.09 their α-chloronaphthalene content varies from 7-50 % by weight.

In view of the high hygroscopicity of heavy water with a concentration of D approaching 100 at.%, conditions of measurement are made more stringent and their accuracy is checked by tests with water containing 99.8 at.%D. All operations with heavy water should be carried out rapidly, avoiding, as far as possible, long contact with the atmosphere.

It was established that for analysis it is necessary to choose a sample of D_2O of not less than 2 ml; when 5 samples were then taken from this 2 ml and dropping time determined by the micro-dropper, the sampling did not affect dropping time (104.5; 104.8; 104.9; 104.5; 104.7 seconds). The dropping time of this water remained constant on storing 3-4 ml for 3 days in a weighing bottle with a closely fitting ground glass lid.

The dropping time of fresh samples of water taken from a vessel containing 500 ml of D_2O over a period of two months was reproducible to within a few tenths of a second. This testifies to the reliability of the measurements carried out with deuterium oxide by the dropping method and to the stability of mixtures of diphenylmethane with α-choronaphthalene.*

Preliminary treatment of the mixtures with heavy water is not necessary. This is confirmed by the constancy of the dropping time of water in freshly prepared mixtures, and in mixtures given a preliminary treatment with heavy water. In order to get accurate results, the mixture should be thermostated an hour before an analysis is made. When measurements are carried out, it is recommended that the capillary of the micro-dropper should be washed out twice with the test water.

On the basis of pyknometric measurements of the density of water, a calibration curve was constructed for analysis of heavy water containing from 98 to 102 at.% of the heavy isotopes of hydrogen and oxygen. The dropping time of such water was, respectively, 172 and 68 seconds.

Analyses carried out in parallel by the drop method, and pyknometrically, respectively agree as shown in the Table:

TABLE

Sample	Dropping time in seconds	Concentration D, at.%	
		dropping method	pyknometric method
1	106.4	99.75	99.74
2	106.8	99.73	99.74
3	107.1	99.73	99.77
4	112.6	99.54	99.54

The conditions and accuracy of work with heavy water containing about 100 at.% D were independently checked by three workers.

SUMMARY

1. New liquids have been suggested for the isotopic analysis of water by the drop method, they are: diphenylmethane for deuterium concentration range 5-27 at.%, and mixtures of diphenylmethane and α-chloronaphthalene for the range 20-100 at.% D. These liquids are characterized by their stability.

2. It has been shown that the drop method can be used with high precision for the analysis of heavy water with deuterium concentrations approaching 100 at.%.

LITERATURE CITED

[1] A. I. Shatenshtein and Ya. M. Varshavsky, J. Anal. Chem. 11, 746 (1956).

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* Data is available which shows that a mixture containing about 50% of α-chloronaphthalene is stable over a period of six months. The stability of the mixtures used for analyzing water with a concentration of 25 and 35 at.% D was checked over a month. The high stability of the mixtures allows them to be used without daily checking by means of standards. Nevertheless, it is obvious that the stability of the mixture will depend on the purity of the reagents used for making the mixtures, and must be checked periodically.

STUDIES IN THE APPLICATION OF COUNTER-CURRENT DISTRIBUTION

PART 2. QUANTITATIVE ANALYSIS OF ISOMERS AND THEIR MIXTURES BY THE METHOD OF COUNTER-CURRENT DISTRIBUTION, TAKING THE ORTHO AND PARA ISOMERS OF CHLOROBENZOIC ACID AS AN EXAMPLE

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The construction of an elementary cell for a counter-current distribution apparatus, which was described in a previous article [1], allows one to get a very sharp separation of phases, whereby it should be possible to increase accuracy during analysis of mixtures of materials of similar properties. In order to establish the accuracy of an apparatus assembled from such cells, a series of experiments were carried out on the separation of synthetic mixtures of ortho- and para- chlorobenzoic acid, taken in various amounts. This example is of interest because exact determination of the ratio of isomers in their mixtures is important for solving many theoretical and practical questions, while, at the same time, it is a fairly complex problem. Successful analysis of such a problem would mean that the apparatus used could be used for studying the quantitative composition of other mixtures which are difficult to separate.

TABLE 1

Comparison of the Efficiency of Different Variants of the Method of Counter-Current Distribution for Mixtures with $K_1 = 1$ and $K_2 = 3$

Index	Apparatus consisting of 20 cells		Apparatus consisting of 60 cells
	normal distribution; 20 transfers	withdrawal of the upper phase; 60 transfers	usual distribution; 60 transfers
Maximum of material with $K_1 = 1$	10 th cell	27 th sampling	30 th cell
Maximum of material with $K_2 = 3$	15 th cell	41 st sampling	45 th cell
Differences between maxima	5 cells	14 samplings	15 cells
Possibility of obtaining pure material with $K_1 = 1$	13.2%	66.2%	74%
Possibility of obtaining pure material with $K_2 = 3$	12%	46.6%	68%

In order to get fuller separation of the mixtures, usual distribution without withdrawing was not used, instead the method of withdrawing the upper phase was used; this latter technique, as is known, permits one to achieve a considerably more efficient separation of mixtures. In order to illustrate this position we have given in Table 1 calculated values characterizing the separation of mixtures of equal amounts of materials with $K_1 = 1$, and $K_2 = 3$, in an apparatus consisting of 20 cells, using the normal distribution technique and the method of withdrawing the upper phases, respectively. For comparison, we also include results of distribution in a 60 cell apparatus.

As can be seen from Table 1, the technique of withdrawing the upper phase is considerably more efficient. Thus, in the example given, the possibility of isolating pure materials with $K_1 = 1$, and $K_2 = 3$ increased 2.6 and 1.8 times, respectively, as compared with that which can be achieved by normal distribution. Finally, increasing the number of primary cells to 60 leads to even greater efficiency of the apparatus; when, however, the same of number of cells are involved, the technique of withdrawing the upper phase has undoubted advantages, as a consequence of which we decided to use it. The construction of our apparatus permits this technique to be used.

Since the components of the mixture to be analyzed were available in a pure form, we made a preliminary study of the most suitable system of solvents since the selection of the latter is of great importance for the success of the counter-current distribution technique. The solvent system should satisfy the following requirements: 1) the partition coefficients of the materials to be separated (K_1 and K_2) should differ as much as possible in the chosen solvent system, or more accurately, their ratio $\beta = K_1/K_2$ should be as large as possible; 2) both partition coefficients should not be simultaneously considerably greater (or considerably less) than unity.* Further, the solvent system should satisfy a number of practical requirements; the system should separate into layers rapidly and completely; the solvent system should not interfere with the method used for identifying the materials; it should not be made up of solvents which are not readily available, which are difficult to purify, or are very volatile, poisonous, or have an odious smell, etc.

For analyzing mixtures of chlorobenzoic acid isomers, systems made of various amounts of the following solvent were used: carbon tetrachloride – methanol – water [2]; chlorobenzene – methanol – water; chloroform – butanol – water; butanol – semi- saturated solution of sodium chloride with 1/15 N phosphate buffer of varying pH. The latter system with a pH of 5.9 proved to be the most convenient.** The chosen system meets all the requirements for the phase system, viz. the ratio of the distribution coefficients of the two isomers $\beta = K_{para}/K_{ortho} = 11.3/2.1 = 5.3$, is large enough to ensure good separation of the isomers; the phases separate into layers rapidly, and completely; the system of solvents is very stable and does not interfere with the indicators for the acids being studied since they are only determined in the upperphase – the butanol phase. It is possible that this system, by appropriate changes in pH, might be suitable for separating other organic acids and bases by the counter-current distribution method.

The amount of chlorobenzoic acid in each sample taken was determined by titration with 0.01 N sodium hydroxide using phenolphthalein as indicator. In order to avoid titration in a two-phase system (aqueous sodium hydroxide and butanol) 5 ml of neutral ethanol was added to each 10 ml of upper phase withdrawn.

Experiments on separation of chlorobenzoic acid isomers were carried out by the method described in our first paper. In order to eliminate errors connected with shifting of the equilibrium of phases already in equilibrium we adopted the following technique. Before starting a test, pure light phase was introduced in the "null" cell of the apparatus (each cell of which contained 10 ml of heavy phase); after this the phases were mixed intensively, the layers allowed to separate, and the light phase transferred into the adjacent cell in the same way as during the distribution process. All these operations with pure upper phase were repeated again several times; only afterwards was the test mixture introduced into the "null" cell. By doing this, pure light phase, already in equilibrium with heavy phase, precedes the distribution front at all times in several of the cells, immediately before the very moment of distribution. On withdrawal of pure light phase it is used for controlling the volumes poured off, and for determining corrections to be applied for titration of pure light phase after distribution.

In order to calculate the accuracy of determination for various ratios of the components, we carried out a series of tests on the distribution, under equal conditions, of mixtures of ortho- and parachlorobenzoic acids in the ratios 1:4 (Fig. 1), 1:1 (Fig. 2), and 1:0.25 (Fig. 3). Not more than 0.1-0.15 g of the mixtures were taken for analysis. Distribution was carried out between equal volumes (10 ml) of light and heavy phases in each cell. In addition, a special experiment was carried out on the distribution for mixtures of isomers at a ratio of 1:1 for volumes of heavy light phases of 10 ml and 5 ml, respectively (Fig. 4).

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* For normal distribution (without withdrawing) best separation is achieved for a given value of β, for $\alpha = K_1 \cdot K_2 = 1$. When the method of withdrawal of the upper phase is used, choice is considerably more complicated since separation is more complete at low values of β; at the same time however, it takes much longer to carry out an analysis, and the concentration of material in an individual cell is cut down.

** pH was determined by the antimony electrode, since determination by other methods is connected with large "salt" errors, since the solution is "half-saturated."

The experiments carried out showed that for all the ratios indicated above for ortho and para chlorobenzoic acid, determinations can be carried out with great accuracy. For determinations of mixtures consisting of 80% para and 20% ortho isomers (Fig. 1), the values actually found were 80.4 and 19.9%, respectively.

For determinations of mixtures composed of 50% of each isomer (Fig. 2), the values found were 50.05% of the para and 49.4% of the ortho isomer. The most difficult mixtures to analyze were ones composed of 20% para and 80% ortho isomer (Fig. 3) since, under the experimental conditions used, para chlorobenzoic acid, whose transfer is more rapid, is not contained in a pure form in any of the samples removed – it was always contaminated with ortho isomer. The amount of ortho isomer was found to be 80.2%, and the amount of para isomer which could only be determined by difference, was 19.8%. In the experiment on separation of mixtures composed of 51% para and 49% ortho isomers, respectively, in which the volumes of light and heavy phases were different (Fig. 4), the values obtained were 51.2 and 49.1%, respectively.

It follows from these results that the accuracy of determination of percentage composition of the isomers in their mixtures was not less than 99% in each case. The high order of accuracy possible on this apparatus is illustrated by the very good agreement between experimental curves and theoretical curves: in all tests (Figs. 1-4), for most points, these curves are so close to each other that differences between them are imperceptible on the graphs; accordingly, in order to give a good idea of the agreement between experimental and theoretical curves, all results relating to the graphs given on Fig. 4 are given in Table 2. This experiment was carried out under the most difficult conditons, since the volume of the light phase (5 ml) was only half of that of the heavy phase (10 ml). Accordingly, the possibility of errors was greater; nevertheless, as the adduced results show, even in this case a high order of accuracy was achieved.

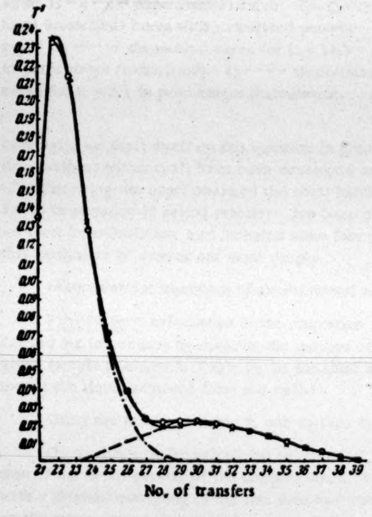

Fig. 1. Distribution of mixtures of the para- and ortho- isomers of chlorobenzoic acid: 1) – × – × – experimental curve; 2) –O – total theoretical curve taking into account calculated percentages; 3) – · – · – · theoretical curve for K = 11.3 in percentages (calculated); 4) – – – – – – theoretical curve for K = 1.1 in percentages (calculated).

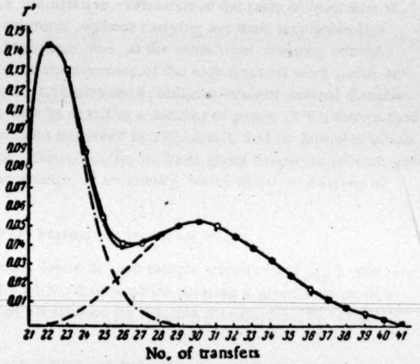

Fig. 2. Distribution of mixtures of para and ortho (50 and 50%) isomers of chlorobenzoic acid: 1) –×–×– experimental curve; 2) –O–O– total theoretical curve with calculated percentages; 3) –·–·– theoretical curve for K = 11.3 in percentages (calculated); 4) – – – theoretical curve for K = 2.1 in percentages (calculated).

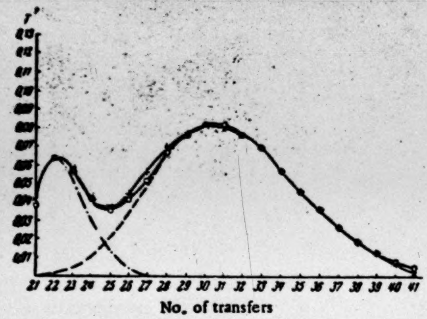

Fig. 3. Distribution of mixtures of para and ortho (20 and 80%) isomers of chlorobenzoic acid: 1) –x–x– experimental curve; 2)–O–O– total theoretical curve with calculated percentages; 3) –·–·– theoretical curve for K = 11.3 in percentages (calculated); 4) –––– theoretical curve for K = 2.1 in percentages (calculated).

Since on decreasing the volume of the upper phase by a half, the effective distribution coefficient (K_{eff}), which is equal to the ratio of the amount of material in the upper phase to that in the lower phase, will also be halved, then in order to bring the value of K_{eff} close to the values of K at which the previous experiments were carried out, it was necessary to increase K. With this object in view the pH was lowered from 5.9 to 5.4; as a result of this the distribution coefficient (K) of para, and ortho isomers, respectively, increased to 20.4 and 3.1, while their ratio (β) changed to a relatively small extent (at pH 5.4, $\beta = 20.4/3.1 = 6.77$, while at pH 5.9, $\beta = 11.3/2.1 = 5.3$).

Halving the volume of the upper phase made K_{eff} equal to 10.2 and 1.55, respectively. This allows one to make a direct comparison of the experimental results obtained for separation of the isomers in a ratio of 1 : 1 at pH 5.9 (Fig. 2) and at pH 5.4 (Fig. 4).

One of the most important merits of the counter-current distribution method is the possibility of its strict mathematical treatment, whereby one can give a quantitative evaluation of the ratio of materials in mixtures without carrying out their separation in a pure form, and at the same time ensuring control over the accuracy of the experimental work itself; accordingly, we shall dwell on this question in greater detail. Calculations in ordinary counter-current distribution (without withdrawal) have been developed and described in detail in a number of papers [3-6]; the method of withdrawing the upper phase, on the other hand, has not been described in such detail, and no formulas which are of importance in actual practice have been published. Consequently, we have given below the scheme which we used for calculation, and included some formulas, not mentioned previously, which allow an analysis of this method to be carried out more simply.

Mathematical treatment of experimental results was carried out in several stages.

First Stage – calculation of the proportion of material found in each sample withdrawn ($T_{exp.}$), was carried out in our case by dividing the number of ml of 0.01 N alkali used for titrating a given volume of a given sample (Column 2, Table 2), by the total amount of alkali used for titrating all samples. (By sample is meant the liquid removed from one cell.)

Using the results in Table 2, one can see that $T'_{21} = 7.0 : 95.3 = 0.0734$; $T'_{22} = 12.8 : 95.3 = 0.1342$, etc.

On the basis of the calculated values of T', an experimental curve can be drawn which gives an indication of the heterogeneity of the samples taken. It is clear from Fig. 4, that in the given case we are dealing with a mixture consisting of not less than two materials with different values of K since there are two maxima on the curve. Nevertheless, it is only by further mathematical treatment that it becomes possible to form an idea of the actual number of components in the mixture, and of the character of these components.

Second Stage – consists in determining the distribution coefficients of the components making up the mixture. For a sufficiently large number of samples, we suggest a simple approximate formula by means of which it is possible to determine K from the maxima

$$K = \frac{R}{N_{max} - R}, \tag{1}$$

where K is the distribution coefficient; N_{max} is the number of sample with the highest content of material; R is the number of the cell from which the sample was withdrawn.

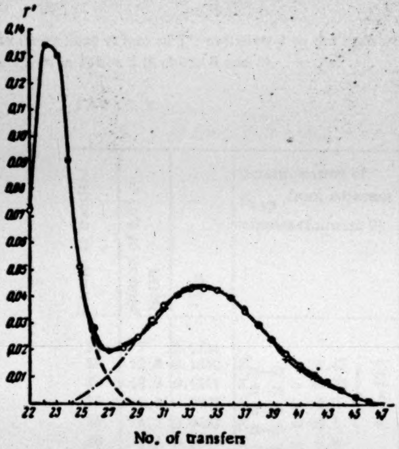

Fig. 4. Distribution of mixtures of para- and ortho- (51 and 49%) chlorobenzoic acid: 1) –×–×– experimental curve; 2)–O–O– total theoretical curve with calculated percentages; 3)–·–·– theoretical curve for K = 10.2 in percentages (calculated): 4)– – – – theoretical curve for K = 1.55 in percentages (calculated).

Using this formula, it is possible to determine the distribution coefficient fairly accurately as long as it is not very large; if the value of K is high (also for checking and getting a more accurate degree of this value), it is necessary to calculate K on the basis of adjacent samples, using the formula previously given in the literature [7]:

$$K = \frac{n-1}{n-R-1} \cdot \frac{T'_{(n-1)}}{T'_n}, \tag{2}$$

where K is the distribution coefficient; n is the number of transfers (including sampling); R is the number of the cell from which sampling was carried out; $T'_{(n-1)}$ and T'_n = the proportion of material in the sample. Determination of K by means of formula (2) should be carried out for all samples, since this enables one to establish accurately the presence of pure components (characterized by a constant value for K) and their mixtures (K is variable). Thus, from the results given in Table 2, it is clear that in samples 21-24, pure material with K_{eff} = 10.2 is present, while in samples 25-30, where K varies, there are present mixtures with various ratios of the materials; starting at the 30th transfer, the second material with K_{eff} = 1.55 is present. To determine K more accurately it is necessary to determine it as the mean of values obtained for the zone of an individual material. In this case, random errors of individual determinations are eliminated.

As an example we have given Table 3 a comparison of the values of K determined by means of formulas (1) and (2), respectively.

As can be seen from these results, there is complete agreement between the values of K for the slow component, as determined by these two methods; this holds true for other cases also, where the maximum is located at a suffieicently large number of transfers from the beginning of the sampling; in such cases there is no need to use formula (2), since determination of K by means of formula (1) is accurate enough and is very simple.

The Third Stage of Mathematical Treatment – calculation of the theoretical values of T' on the basis of the values found for K, can be carried out by means of the general formula (3)

$$T'_{n,R} = \frac{(n-1)!}{R!\,(n-1-R)!} \cdot \left[\frac{1}{k+1}\right]^n \cdot K^{R+1}. \tag{3}$$

For the most common case where calculation of the values of T' starts with the first sample from the last cell (i.e., when R = n – 1), the coefficient $\frac{(n-1)!}{R!\,(n-1-R)!}$ is equal to unity, as a result of which, formula (3) is simplified and assumes the following form:

$$T'_{n,R} = \left(\frac{K}{k+1}\right)^{R+1}. \tag{4}$$

Calculation of T' for subsequent samples can be conveniently carried out by means of the published formula [7]:

$$T'_{n,\,R} = \frac{n-1}{n-R-1} \cdot \frac{i}{k+1} \cdot T'_{(n-1)} \,. \qquad (5)$$

The theoretical values of T', calculated on the basis of the experimental values of K, using these formulas, are given in Table 2 (Colums 5 and 6).

TABLE 2

Number of transfers	Amount of 0,01 N NaOH	T'_{exp}	Determination of K_{exp} from adjacent samples (formula 2)		T'_{theor} calculated on the basis of values found for K		T'_{theor} for % found		Tot. value of T_{theor} from calculated percentages	Deviation between experimental and theoretical results
					For $K = 10.2$	For $K = 1.55$	From T' at K = 10,2	From T' at K = 1,55		
21	7	0.0734			0.1402		0.0715		0 0715	+0.0019
22	12.8	0.1342	$K_{21-22} = 10.45$	$K = 10.2$	0.2630		0.134		0.134	+0.0002
23	12.5	0.1311	$K_{22-23} = 10.25$		0.2583	0.0010	0.132		0.132	−0.0009
24	8.65	0.0907	$K_{23-24} = 10.0$		0.1768	0.0030	0.0902	0.0014	0.0916	−0.0009
25	4.7	0.0492	$K_{24-25} = 10.1$		0.0947	0.0072	0.0483	0.0035	0.0518	−0.0026
26	2.3	0.0241	$K_{25-26} = 9.2$		0.0423	0.0142	0.0216	0.0069	0.0285	−0.0044
27	1.9	0.0199	$K_{26-27} = 4.3$		0.0164	0.0241	0.0083	0.0118	0.0201	−0.0002
28	2.15	0.0225	$K_{27-28} = 2.4$		0.0056	0.0368	0.0029	0.0180	0.0209	+0.0016
29	2.4	0.0251	$K_{28-29} = 2.13$		0.0017	0.0506	0.0009	0.0248	0.0257	−0.0006
30	2.9	0.0304	$K_{29-30} = 1.67$		0.0005	0.0639		0.0315	0.0315	−0.0011
31	3.4	0.0356	$K_{30-31} = 1.56$	$K_{av} = 1.55$		0.0757		0.0374	0.0374	−0.0018
32	4.0	0.0419	$K_{31-32} = 1.4$			0.0830		0.0409	0.0409	+0.0010
33	4.2	0.0440	$K_{32-33} = 1.54$			0.0868		0.0425	0.0425	+0.0015
34	4.15	0.0435	$K_{33-34} = 1.56$			0.0868		0.0425	0.0425	+0.0010
35	4.1	0.0429	$K_{34-35} = 1.47$			0.0865		0.0424	0.0424	+0.0005
36	3.9	0.0408	$K_{35-36} = 1.46$			0.0791		0.0388	0.0388	+0.0020
37	3.5	0.0367	$K_{36-37} = 1.51$			0.0698		0.0342	0.0342	+0.0025
38	2.8	0.0293	$K_{37-38} = 1.7$			0.0596		0.0292	0.0292	+0.0001
39	2.3	0.0241	$K_{38-39} = 1.58$			0.0493		0.0243	0.0243	−0.0002
40	1.65	0.0173	$K_{39-40} = 1.86$			0.0397		0.0194	0.0194	−0.0021
41	1.3	0.0136	$K_{40-41} = 1.54$			0.0311		0.0148	0.0148	−0.0013
42	1.0	0.0105	$K_{41-42} = 1.54$			0.0238		0.0117	0.0117	−0.0012
43	0.8	0.0084	$K_{42-43} = 1.4$			0.0178		0.0087	0.0087	−0.0003
44	0.6	0.0063	$K_{43-44} = 1.5$			0.0133		0.0065	0.0065	−0.0002
45	0.2	0.0021				0.0047		0.0023	0.0023	−0 0002
46	0.15	0.0016				0.0032		0.0015	0.0015	+0.0001
47	0.1	0.001				0.0023		0.0010	0.0010	0,0000
Total	95.3									

The Fourth Stage of the Mathematical Treatment – calculation of the percentage content of the mixture components, is, in our opinion, more expediently carried out, not on the basis of individual points (see e.g., [3], but by taking all the cells together which have a constant value of K, i.e., containing pure material. For this, it is necessary to take the sum of T'_{exp} for all those samples where K is constant, divide it by the sum of T'_{theor} calculated for the same samples, and multiply the ratio by 100.

$$\% = \frac{\Sigma T'_{exp}}{\Sigma T'_{theor}} \cdot 100. \qquad (6)$$

In the experiment under consideration, the para isomer content should be found by taking the sum of T' in the range 21-24 transfers (equal to 0.4275), and dividing it by the sum of T'_{theor} for the same transfers (equal to 0.8383); this gives a value for the para isomer content of 51.2%. Similarily, for the ortho isomer content, the sum of $T_{exp.}$ for the transfers 29-44 (0.4275) is divided by the sum of T_{theor} (equal to 0.8711); the percentage content of the ortho isomer in this case is 49.1.

TABLE 3

Effective Distribution Coefficients of Chlorobenzoic Acid Isomers for a Phase Ratio of 1: 2

Isomer	Values of K_{eff} calculated by means of formula: (1)	(2)
Para	10.0	10.2
Ortho	1.546	1.55

Calculation of the percentage content of the components of the mixture can, of course, be carried out on the basis of individual points, the mean of the results obtained being taken. This method, however, is not so reliable, since points at which the samples contain a large amount of material respectively, will have an equal effect on the calculated mean content. All the same, such a method of calculation is interesting, since it allows one to evaluate how much the values for the percentage composition, calculated by means of these points, differ from each other and to evaluate the probable mean arithmetic error.

The probable mean arithmetic error of a series of independent determinations can be calculated by means of the formula [8]:

$$\rho_A = \pm 0.6745 \sqrt{\frac{\Sigma_\varepsilon^2}{n(n-1)}}, \qquad (7)$$

where ρ_A is the probable mean arithmetic error; Σ_ε^2 is the sum of the squares of the deviations of individual measurements from the mean arutgnetuc vakye; n is the number of measurements.

TABLE 4

Comparions of Ratios Taken and Found for Chlorobenzoic Acid Isomers

Taken		Found			
para	ortho	ratio of the sums T'		means of all determinations in %	
		para	ortho	para	ortho
80	20	80.4	19.99	80.3 ± 0.85	19.65 ± 0.17
50	50	50.05	49.4	50.05 ± 0.1	49.7 ± 0.15
20	80	—	79	—	79.2 ± 0.2
51	49	51.2	49.1	51.32 ± 0.38	49.6 ± 0.27

As can be seen from Table 4, the percentage contents of the isomers, determined by distribution of their mixtures (see Figs. 1-4), are in good agreement with the given ratios and with those found by the method described above; the probable mean arithmetic error did not exceed 1% in any case, while the values found for the percentage content of the isomers in the mixture were very close to those taken. Although the calculated values of the percentage content of the mixtures are in good agreement, the first method is preferable since it is more objective.

This completes the mathematical treatment carried out with the object of establishing the composition of the mixture, but for controlling the experimental accuracy it is necessary to carry mathematical treatment further; i.e., one must calculate the over-all theoretical curve which is the sum of the theoretical curves for the individual components of the mixtures, calculated on the basis of percentages found (See Figs. 1-4). A judgement of the accuracy of an experiment can be formed by comparing columns 9 and 3 in Table 2. The difference between which is given in column 10. Deviations of the experimental results obtained from the total theoretical values are insignificant so that the accuracy of determining the percentage content of the isomers in their mixtures is high.

Unfortunately, it is difficult to compare the degree of accuracy of an analysis carried out by means of our apparatus with that carried out on other apparatus, since in most cases, the authors do not give enough details, which means that the general form of the curves is restricted. If one goes by the numerous published curves (See, e.g., [9]) in which theoretical and experimental results are compared, it seems, as a rule, that there are greater deviations between theory and practice in these results than in ours. The results given in some individual articles do not give a complete picture of the experiment. Thus, in Raymond's work no results are given which allow one to compare the amount of individual materials taken with that actually determined experimentally. Nevertheless, the total amount of acids found amounts to only 94.8% of the calculated amounts; thus, even in this case, the accuracy of the work is appreciably lower than in ours. Deviations of individual determinations in the cited work in some cases amount to more than 25%. In one of the review articles, Golumbic [3], without adducing any material, evaluates the mean error of the method of counter-current distributions as 3-5%. Presumably, the increase in accuracy of our experiment is connected with improvements in construction of the primary cell, which enables one to get a better separation of the phases, and possibly with the more objective method of calculating the percentages of the components. With this increase in the accuracy of the counter-current distribution technique, it should be possible to widen its field of application to solving a number of general chemical problems, in which it is necessary to determine materials of similar properties in their mixtures accurately. It seems to us, e.g., that it would be expedient to use this method for quantitative determination of isomers formed under different experimental conditions for establishing the comparative strength of the orientating effects of substitutents, and other questions, whose solution without resorting to this new quantitative technique is complicated, or, in general, cannot be realized.

SUMMARY

1. It has been shown experimentally that by using an apparatus for counter-current distribution consisting of 21 primary cells, whose construction has been described before, and using the technique of removing the upper phase, it is possible to carry out quantitative determination of mixtures of ortho- and parachlorobenzoic acid on samples of 0.1 - 0.2 g.

The error of determination is very small, and did not exceed 1% in any one case; as a rule it was much smaller.

2. A number of techniques have been worked out for increasing the accuracy of counter-current distribution, and the method of withdrawing the upper phase has been simplified. The advantages of this method have been demonstrated.

3. Mathematical analysis of the counter-current distribution method, when the technique of the withdrawal of the upper phase is used, has been made more accurate.

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MICRO AND SEMIMICRO DETERMINATION OF NITROGEN BY HYDROGENATION OF ORGANIC MATERIALS

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Determination of nitrogen as ammonia obtained as the result of hydrogenating organic compounds has been known for more than 25 years; nevertheless the literature devoted to this method is very scant [1-5], and the method has not been widely used. The method is known in macro, semimicro, and micro modifications and consists of slow heating of an aliquot of test material mixed with nickel; the vapors formed are then passed in a slow stream of hydrogen (1 ml/minute) over a nickel catalyst heated to 300°. The ammonia formed is absorbed with acid, excess of which is titrated with alkali. The necessity for slow decomposition and low gas flow rate has been emphasized by all authors.

The introduction into elemental analysis of new principles of decomposition of organic materials, and the successful application of these principles to reductive decomposition as well [6-7], led us to develop a micro determination of nitrogen, by hydrogenation of organic materials, using a high gas flow rate and rapid pyrolytic decomposition of samples [8].

The method we have developed reduces in essence to the following: the aliquot of nitrogen-containing organic material is subjected to rapid thermal decomposition in a hydrogen atmosphere, and the decomposition products in admixture with excess hydrogen are then passed over an iron catalyst at a gas flow rate of 35-40 ml/minute. Under these conditions, the nitrogen present in the organic material is quantitatively converted into ammonia, which is absorbed by a standard solution of potassium biiodate and determined iodometrically.

Method of Decomposition. All analysts working with hydrogenation methods use techniques for decomposing materials such that a mixture of the vapors of the test material and its decomposition and hydrogenation products arrives at the catalyst, while the basic mass of the material does not undergo any fundamental changes before it gets to the catalyst. With this method of decomposition which we shall call "evaporation" we should like to contrast pyrolytic decomposition; in the latter, it is not the vapors of the test material which pass over the catalyst, but very reactive decomposition products formed from the test material at high temperatures.

During hydrogenation of various organic compounds using the technique of pyrolytic decomposition, we succeeded, in a matter of minutes, in achieving complete removal of nitrogen as ammonia (Table 1). When the "evaporation" method was used, the results obtained were low.

Another essential advantage of pyrolytic decomposition over "evaporation" is more complete hydrogenation of material to gaseous products, with consequent drop in the amount of carbon and resin formed during hydrogenation. When any carbon does happen to form, it settles out only on the inner surface of the quartz test tube in which the aliquot has been placed, while the decomposition tube, and what is particularly important, the catalyst, both remain clean. The catalyst showed no signs of poisoning after 100-130 experiments on hydrogenation with pyrolytic decomposition of the samples had been carried out; when the "evaporation" technique was used, on the other hand, the catalyst was rapidly covered with a layer of carbon, and it had to be regenerated after a few analyses.

Catalyst. Instead of the classical catalyst for hydrogenation reactions – nickel – we used the specific catalyst for ammonia synthesis – iron; the optimum operating temperature of the latter is 400°, which is approximately 100° higher than that of nickel catalysts. The possibility of carrying out destructive hydrogenation at 400° instead of 300° is an essential advantage during the analysis of thermostable materials such as carbazole (Table 2).

TABLE 1

Determination of Nitrogen by Rapid Hydrolysis of Samples

Material	Sample weight in mg	Duration of test in min		Nitrogen in %	
		decomposition only	decomposition and purging	found	difference
Methylbenzamide	3.023 3.965	3.5 4.5	7 7.5	10.24 10.38	−0.12 +0.02
p-Aminoacetophenone	3.497 3.100	4 4	7 7	10.58 10.55	+0.22 +0.19
Diphenylurea	5.083	5	12	13.26	+0.06
Triphenylguanidine	5.570 4.180	6 7	15 15	14.63 14.65	+0.01 +0.03
Ammonium oxalate	3.030	5	14	19.55	−0.16
Oxamide	3.490	8	20	31.98	+0.11
Carbazole	3.210 3.575	5 6	10 12	8.25 8.45	−0.13 +0.07

The same lot of catalyst can be used for over 100 analyses without any loss of activity.

Determination of Ammonia. Ammonia formed as the result of hydrogenation was determined iodometrically, using a standard solution of potassium biiodate for absorbing the ammonia. Potassium biiodate is well known in analytical practice [9]; it is readily prepared in a pure form, and keeps well both in the form of crystals, and also in dilute solutions. Excess biiodate can be determined either by titrating the H^+ of the acid salt with alkali, or determination of the iodine liberated on addition of KI; the iodine, the amount of which is equivalent to the amount of hydrogen ions in the acid salt, is back titrated with sodium thiosulfate. Comparison of results of acidimetric and iodometric titration of 0.02 N solutions of potassium biiodate showed that the latter gives more accurate results (Tables 3 and 4).*

Field of Application of the Method. The method is applicable to the analysis of amino compounds, heterocyclic compounds, and also to individual representatives of various classes of nitrogen containing materials (Tables 5,6).

We did not confine ourselves to analysis of materials containing C, H, O, and N, but investigated the possibility of determining nitrogen in the presence of sulfur. Ter-Meulen [1], observes that in the case of analysis of sulfur compounds, the nickel catalyst must be replaced after each determination. We established that poisoning of iron catalysts does not occur immediately, but only after about 15 mg of hydrogen sulfide has passed over the catalyst; this amount of hydrogen sulfide corresponds to that formed on hydrogenation of about 25 samples of sulfur compounds containing about 15% sulfur, for an average weight of 4 mg per sample. If, however, the hydrogen sulfide is held back in the decomposition zone by mixing test sample with five times its amount of reduced nickel,** one can eliminate the poisoning effect of hydrogen sulfide on the iron catalyst.

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* We have also successfully used iodometric titration of excess biiodate, after absorption of ammonia, for micro- and semimicro Kjeldhal determination of nitrogen.

** Reduced iron was not used for mixing with the sample, since such iron is pyrophoric and clinkers readily. The nickel is reduced in a stream of hydrogen and is stored under carbon dioxide.

Actually, when aliquots of sulfur compounds, mixed with reduced nickel, were subjected to hydrogenation in a tube with a platinum catalyst, and the sulfur determined in the gaseous decomposition products by means of our method [6, 10], we found that hydrogen sulfide is practically quantitatively held back by the nickel, and only traces succeed in getting to the absorbers. Consequently, when materials containing sulfur are decomposed after addition of reduced nickel to the sample, only negligible amounts of hydrogen sulfide pass over the catalyst, and poisoning only occurs after a very long time. Thus, we carried out 23 nitrogen determinations in materials containing sulfur, with the same catalyst. The results for determination of nitrogen in the presence of sulfur which are given in Table 5 were also obtained with one lot of catalyst. Thus, this method is also applicable to materials containing C, H, O, N, and S.

TABLE 2

Determination of Nitrogen in Carbazole (Sample weight 3-5 mg; nitrogen content 8.38%)

Catalyst	Operating temperature of the catalyst	Nitrogen in %	
		found	difference
Nickel	320	7.64	−0.74
		7.70	−0.68
	375	7.63	−0.75
		7.19	−1.19
		7.71	−0.67
Iron	300	7.39	−0.99
		7.50	−0.88
	400	8.33	−0.05
		8.38	−0.10
		8.40	+0.02

TABLE 3

Titration of Potassium Biiodate with Alkali (5 ml of 0.02 N $KH(IO_3)_2$ and 1 ml of 10% KI solutions used)

KOH used in ml	Deviation for one titration in ml
5.000	0.000
5.005	0.005
5.005	0.005
5.000	0.000
5.000	0.000
5.000	0.000
4.995	0.005
4.995	0.005
5.000	0.000
5.005	0.005
4.995	0.005
4.995	0.005
Mean 5.000	Mean 0.003

TABLE 4

Titration of Potassium Biiodate with Thiosulfate (5 ml of 0.02 N $KH(IO_3)_2$ and 1 ml of 10% KI solutions used)

$Na_2S_2O_3$ used in ml	Deviation for one titration in ml
5.000	0.000
5.000	0.000
5.000	0.000
5.000	0.000
4.995	0.005
4.995	0.005
5.000	0.000
4.995	0.005
4.995	0.005
5.000	0.000
5.000	0.000
5.000	0.000
Mean 5.000	Mean 0.002

This method is applicable to samples differing widely in weight, of materials containing any amount of nitrogen; this distinguishes it from the Dumas gasometric micro determination, in which the weight of sample taken depends on the nitrogen content. Without modifying the method at all, one can work with sample weights of 2.5 to 20 mg. For high nitrogen contents and large sample weights, it is recommended that 0.05 N solutions be used instead of 0.02 N. Results for semimicro determinations of nitrogen, carried out on a micro apparatus using a semimicro balance and an analytical balance, are given in Tables 5 and 6.

Apparatus. The apparatus was the same as that used for determination of sulfur by hydrogenation [6, 11, 12]. It consists of a Kipps apparatus used for producing hydrogen, two wash bottles, a screw clip (better still, one fitted with a micrometric screw) or a tap with threads for regulating the gas flow, a quartz tube for hydrogenation fitted with a ground glass outlet and two glass receivers also connected to it via ground glass joints, an open electric oven type MA2-20, a gas burner, an aspirator, and a 1 liter measuring cylinder. In addition the following apparatus is necessary: 2 micro burets with a capacity of 10 ml, several 100 ml conical flasks with ground glass stoppers, a tube with a long handle for taking samples during establishment of the titer, and quartz tubes 65 mm long for the samples.

TABLE 5

Determination of Nitrogen in Samples of Different Weights

Test material	Sample weight in mg	0.02 N $KH(IO_3)_2$ used in ml	Nitrogen in %	
			found	difference
Ammonium oxalate	3.710*	2.605	19.67	—0.04
$C_2H_8O_4N_2 \cdot H_2O$; 19.71% N	5.259*	3.690	19.66	—0.05
Ethyl oxamate	3.224*	1.380	12.02	+0.05
$C_4H_7O_3N$; 11.97% N				
p-Phenylenediamine	3.836*	3.530	25.78	—0.13
$C_6H_8N_2$; 25.91% N	3.556*	3,290	25.92	+0.01
p-Aminoacetophenone	2.908*	1.075	10.36	—
C_8H_9ON; 10.36% N	4.103*	1.510	10.31	—0.05
Triphenylguanidine	3.352*	1.740	14.54	—0.08
$C_{19}H_{17}N_3$; 14.62% N	3.831*	1.980	14.48	—0.14
Methylbenzamide	3.405*	1.260	10.37	+0.01
C_8H_9ON; 10.36% N	3.570*	1.315	10.32	—0.04
α-Aminopyridine	4.382*	4.620	29.54	—0.23
$C_5H_6N_2$; 29.77% N	3.270*	3.460	29.64	+0.13
Dipyridylurea	3.685*	3.445	26.19	+0.03
$C_{11}H_{10}ON_4$; 26.16% N	4.085*	3.795	26.02	—0.14
6,6-Dicarbethoxy-5,6,13,14-tetrahydro-1,2-benzophenanthridine	2.971*	4.070	3.84	+0.09
$C_{23}H_{23}O_4N$; 3.73% N				
Carbazole	3.753*	1.120	8.36	—0.02
$C_{12}H_9N$; 8.38% N	4.248*	1.275	8.41	+0.03
Anthranilic acid	10.39 **	3.78	10.19	—0.03
$C_7H_7O_2N$; 10.21% N	8.55 **	3.13	10.25	+0.04
p-Aminoacetophenone	11,65 **	3.34	10.44	+0.08
C_8H_9ON; 10.36% N	11,71 **	3.36	10.41	+0.05
Ethyl oxamate	12.58 **	5.33	11.88	—0.09
$C_4H_7O_3N$; 11.97% N	11.40 **	4.82	11.85	—0.12
Methylbenzamide	10.79 **	4.02	10.40	+0.04
C_8H_9ON; 10.36% N	13.57 **	5.10	10.53	+0.17
Diphenylurea	10.33 **	4.92	13.34	+0.14
$C_{13}H_{12}ON_2$; 13.20% N	11.31 **	5.31	13.15	—0.05
Carbazole	12.19 **	3.64	8.37	—0.01
$C_{12}H_9N$; 8.38% N	12.94 **	3.86	8.35	—0.03
Ammonium oxalate	8.27 **	5.83	19.75	+0.04
$C_2H_8O_4N_2 \cdot H_2O$; 19.71% N	7.65 **	5.35	19.60	—0.11
o-Toluolsulfamide	3.792*	1.085	8.02	—0.16
$C_7H_9O_2NS$; 8.18% N	3.463*	0.995	8.05	—0.13
	4.113*	1.250	8.17	—0.01
Michler's thioketone	5.030*	1.795	10.00	—
$[C_6H_4(CH_3)_2N]_2CS$; 10.00% N	3.080*	1.120	10.19	+0.19
p-Toluolsulfamide	5.324*	1.518	7.99	—0.19
$C_7H_9O_2NS$; 8.18% N	4.456*	1.273	8.00	—0.18
The amide of 2,5-dimethyltetrahydro-1-thiopyrane-4-hydroxy-4-acetic acid	3.403*	0.825	6.79	—0.10
$C_9H_{17}O_2NS$; 6.89% N	3.019*	0.745	6.91	+0.02
The anilide of 2,5-dimethyl-1-thiopyrane-4-hydroxy-4-acetic acid	5.330*	0.942	4.94	+0.10
$C_{15}H_{17}O_2NS$; 4.84% N	5.462*	0.975	5.01	+0.17

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* Samples were weighed on a micro balance with an accuracy of 0.002 mg.

** Samples were weighed on a semi-micro balance with an accuracy of 0.01 mg.

The following reagents are required: ferric nitrate, nickel nitrate or formate, crystalline potassium biiodate, potassium biiodate 0.02 N solution, 0.02 N sodium thiosulfate, 10% solution of potassium iodide, and 1% starch solution.

Preparation of Titrant Solutions. Potassium biiodate solution was prepared from the salt which had been recrystallized three times. 7.799 g of the biiodate was taken for preparation of 1 liter of 0.02 N solution. Thiosulfate solution was prepared by diluting 0.1 N thiosulfate.

Standaridization. Crystalline potassium biiodate is the most suitable material for standardizing the thiosulfate.

When standardization is carried out in a neutral medium, it is permissible to take large amounts of salt (50-60 mg) and thereby eliminate errors in weighing. Thiosulfate can also be standardized by means of potassium iodate (5-6 mg) or sublimed iodine (18-20 mg). In the latter case, the weights were taken in micro bottles with ground glass lids, containing 1-2 drops of a concentrated aqueous solution of potassium iodide. Standardization by all three methods gave results in good agreement with each other. Potassium biiodate was standardized with the thiosulfate. The thiosulfate was checked every 5-7 days.

TABLE 6

Test material	Sample weight in mg*	Amount of $KH(IO_3)_2$ used in ml	Nitrogen in %	
			found	difference
p-Aminoacetophenone C_8H_9ON; 10.36% N	16.70	2.49	10.43	+0.07
	14.30	2.14	10.48	+0.12
Methylbenzamide C_8H_9ON; 10,36% N	14.40	2.15	10.46	+0.10
	12.20	1.82	10.45	+0.09
Diphenylurea $C_{13}H_{12}ON_2$; 13.20% N	14.65	2.79	13.34	+0.14
	13.75	2.63	13.40	+0.20
o-Aminopyridine $C_5H_6N_2$; 29,77% N	8.85	3.76	29.76	−0.01
	12.10	5.17	29.92	+0.15
Dipyridylurea $C_{11}H_{10}ON_4$; 26.16% N	9.85	3.70	26.31	+0.15
	9.60	3.59	26.19	+0.03
p-Phenylenediamine $C_6H_8N_2$; 25.91% N	11.45	4.27	26.11	+0.20
	12.45	4.62	25.99	+0.08
Phenylurea $C_7H_8ON_2$; 20,58% N	12.90	3.81	20.69	+0.11
	8.40	2.49	20.76	+0.18
Ammonium oxalate $C_2H_8O_4N_2 \cdot H_2O$; 19.77% N	14.55	4.11	19.78	+0.07
	9.85	2.79	19.84	+0.13
1,2-Dimethyl-4-ethinyl-4-hydroxydecahydroquinoline $C_{13}H_{21}ON$; 6.76% N	13.05	1.26	6.76	—
	13.85	1.33	6.73	−0.03
1-Ethyl-2-methyl-4-piperidone $C_8H_{15}ON$; 9.92% N	9.45	1.33	9.89	−0.06
	7.25	1.03	9.95	+0.03

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* Samples were weighed on an analytical balance with an accuracy of 0,05 mg.

Preparation of Catalyst. Ferric nitrate is fused in its water of crystallization, the water is then removed, and the material is heated to dryness, next it is calcined until fumes of nitric oxide cease to be evolved; it is finally ground in a mortar to give lumps of 1-3 mm in size, which are sieved free from dust, and loaded into the decomposition tube to give a layer 10 cm long, such that the layer in the tube is in the middle of the electric oven; the layer is held in position by two plugs of asbestos fiber. In the remaining, empty part of the tube, between the catalyst layer and the quartz outlet, is placed a quartz or glass rod, whose diameter is slightly less than that of the decomposition tube. Heated gases, on coming out of the catalyst layer, then proceed along the tube at a high velocity, and only a negligible amount of condensation of moisture on the tube walls is observed.

The catalyst is reduced at 475-500° in a rapid stream of hydrogen (gas flow about 100 ml/minute [13]). Reduction of catalyst takes 10-12 hours. Reduction is complete when no more moisture condenses on the cold parts of the tube. When they are not in use, tube plus catalyst are left under a hydrogen pressure.

Analytical Procedure. The layer of catalyst in the decomposition tube is heated with the electric oven to 400-420° (thermocouple control); 5-7 ml of 0.02 N $KH(IO_3)_2$ is run into the receiver from a micro buret, and the receiver connected via the ground glass joint to the outlet of the decomposition tube, while the other end of the receiver is connected to the aspirator. The sample, in the usual quartz test tube, is placed in the decomposition tube at a distance of 2-3 cm from the electric oven, while the aspirator tap is closed and the Kipps apparatus tap is open. The tube is then closed, and the aspirator tap opened slowly (in order not to blow any liquid out of the receiver), the hydrogen flow is adjusted to 30-40 ml/minute, and a burner placed under the open end of the quartz test tube containing the sample. Decomposition is carried out for an average of 7-10 minutes. 200-400 ml of hydrogen is then passed through the tube, while the burner is moved along to the closed end of the tube.

While purging is being carried out (not more than 10 minutes) the part of the tube between the quartz test tube and the oven is calcined; finally, all the tube is heated from the point of hydrogen entry up to the electric oven; the aspirator tap is then turned off, the receiver is disconnected, and in its place is fitted a second receiver filled ready for the next determination; the whole setup can then be left until one is ready to do the next analysis.

The contents of the receiver are transferred to a 100 ml conical flask fitted with a ground glass stopper, the receiver is then rinsed three times with cooled distilled water, the wash liquors being added to the liquid already in the conical flask; 1 ml of 10% potassium iodide solution is added to the contents of the flask, the flask is stood for 5 minutes in ice water and the iodine liberated titrated with thiosulfate. One determination usually takes about 30 minutes.

SUMMARY

1. Micro- and semicro methods have been developed for determination of nitrogen by hydrogenation of nitrogen-containing organic materials; these are based on rapid pyrolysis of the material in a hydrogen atmosphere, when the nitrogen is converted into ammonia over an iron catalyst, the ammonia being determined iodometrically.

2. The method can be used for analysis of amino compounds and heterocyclic compounds containing C, H, O, N, and S. One determination takes about 30 minutes.

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DETERMINATION OF ELEMENTAL SULFUR IN PETROLEUM AND PETROLEUM PRODUCTS BY A POLAROGRAPHIC METHOD

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Academician Nametkin as long ago as 1943 [1], criticized existing methods for the group analysis of sulfur compounds contained in light petroleum fractions. He showed that metallic mercury, added for selective removal of free sulfur, partially reacts with mercaptans. The drawbacks characteristic of modern methods of group analysis of sulfur compounds, have been made clear in recent years in a number of papers devoted to the direct determination of both sulfur and its organic compounds, which are contained not only in the benzine fractions, but also in a heavier petroleum fractions.

Gerber and Shusharina [2], have developed a method for the polarographic determination of free sulfur and disulfides in benzine and kerosene. These research workers have demonstrated the possibility of carrying out a direct quantitative determination of free sulfur in the presence of organic sulfur compounds. In later papers, Hall [3,4], and also Harrison and Harvey [5], reported determination of elemental sulfur in light petroleum fractions.

In 1952-1953 it was established that it is possible to determine elemental sulfur in crude oil in the Chemical Section of the Bashkirsky Branch of the Acad. Sci. USSR.

Just at the time that this work was being concluded and practical results were being obtained, an article appeared which dealt with the polarographic determination of elemental sulfur in American petroleum [6]. Polarographic determination of elemental sulfur in the article by the American research workers was carried out under different conditions from ours. Further, the American workers did not take into account the effect of sulfur compounds on the polarographic wave of elemental sulfur. Our experiments showed that mercaptans can distort results of elemental sulfur determination.

EXPERIMENTAL

Studies were carried out on a model M-8-2000 visual type polarograph of the Gorky Institute, using a type GZS-47 mirror galvanometer. The electrolytic cell was placed in an air thermostat which kept the temperature constant with an accuracy of ± 0.5°. The reference electrode was a calomel half-element prepared according to published data [7].

Sulfur which had been twice recrystallized from benzene and dissolved in desulfurized petroleum fractions from the Tulmazinsky field was used for the investigation. The sulfur solutions were added to the "polarographic solution", serving as supporting electrolyte. The latter consisted of benzene (50.0 wt.%), 90% ethanol (47.0 wt.%), water (2.0 wt.%), glacial acetic acid (0.3 wt.%), and crystalline sodium acetate (0.7 wt.%). It is possible to dissolve up to 10% (by volume) of the petroleum fractions. Hydrogen was bubbled through all solutions for 20 minutes.

Polarograms obtained for sulfur dissolved in a 175-200° fraction are given in Fig. 1. It follows from these curves that the point at which elemental sulfur starts to be reduced depends on its concentration in solution, and lies within the range -0.5 to -0.7 v. The position of the maximum on the curves also depends on sulfur concentration and changes within the range -0.8 to -1.3 v. This relation between the point at which the sulfur starts to be reduced and concentration, and the relation between the half-wave potential and sulfur concentration in solution, which we observed, have also been noted in the work of other investigators.

For a certain concentration range there is a linear relation between the height of the polarographic wave, expressed in μ A, and sulfur concentration in solution, expressed in wt.% (Fig. 2 and Table 1). We took as wave height for sulfur determination, the distance from the abscissa to the position of the minimum on the polarographic curve, and arbitrarily denoted it by I_d.

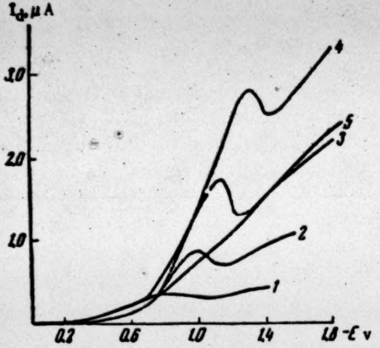

Fig. 1. Polarograms for elemental sulfur dissolved in petroleum fractions of the range 175-200°: 1) sulfur concentration 0.00106 wt.%; 2) sulfur concentration 0.00212 wt.%; 3) sulfur concentration 0.00425 wt.%; 4) sulfur concentration 0.00850 wt.%; 5) curve for supporting electrolyte.

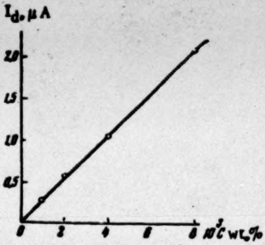

Fig. 2. Relation between diffusion current and concentration of elemental sulfur in the 175-200° petroleum fraction.

Since it was difficult to achieve complete removal of oxygen from solution by blowing hydrogen through the latter, the polarographic curves which we got were distorted somewhat by oxygen maxima. Consequently, for the case under discussion, the relation between i_d and concentration is expressed by the equation $i_d = 317\ c$ (1).

Gerber and Shusharina [2], during their studies of the polarographic determination of sulfur contained in petroleum products, observed an "upper limit" for sulfur concentration, above which the relation between diffusion current and concentration was not linear. The authors attributed this to appreciable reaction between sulfur and the metallic mercury of the electrolytic cell.

For solutions of sulfur in 175-200° fractions which we studied, this "upper limit" was found to be 0.01%. Nevertheless, by diluting the test solution the requisite number of times, it is possible to determine the sulfur content of fractions with a higher sulfur content than the "upper limit" concentration. The lower limit concentration at which sulfur can be determined depends on the sensitivity of the polarograph, and the solubility of the test solution in the supporting electrolyte. In our experiments, the lower limit proved to be 0.002 wt.% in the test solution.

Solutions of sulfur dissolved in 250-275° fractions, gave polarograms qualitatively similar to those obtained for solutions of sulfur in 175-200° fractions. Nevertheless, the quantitative relation between height of the polarographic wave and sulfur concentration in solution (Table 1) is expressed by another equation $i_d = 173\underline{c}$ (2).

For polarographic determination of elemental sulfur dissolved in 300-340° fractions, it was established that the relation between wave height and sulfur concentration is expressed by the equation $i_d = 142\ c$ (3), in which the proportionality coefficient has an even lower value than in either of the preceding equations (Table 1).

In addition to determining sulfur added artificially to petroleum fractions, we also carried out polarographic determinations of synthetic solutions of sulfur in crudes (Table 1). The supporting electrolyte which we used for polarographic determination of sulfur in the petroleum fractions, proved unsuitable for determination

TABLE 1

Relation between Proportionality Constant K and Boiling Range of Fraction in which the Elemental Sulfur was Dissolved*

Boiling range of fraction in °C and sulfur concentration in the original solution in wt.%	Concentration of elemental sulfur in the polarographic cell in wt.%	Height of the minimum on the polarographic wave in mm	I_d in μA	$K = \frac{i_d}{c}$
175—200	0.00850	61	2.56	301
	0.00425	31	1.30	306
0.425	0.00212	17	0.72	340
	0.00106	8	0.34	321
			Mean	317
250—275	0.0044	18	0.76	173
	0.0022	9	0.38	173
0.420	0.0011	4.5	0.19	173
			Mean	173
300—340	0.0150	50	2.10	140
	0.0100	32	1.35	135
0.470	0.0050	17	0.71	142
	0.0025	9	0.38	152
			Mean	142
Petroleum in benzene	0.00036	30	0.29 ***	806
	0.00024	21	0.20 ***	833
1 : 4	0.00012	10.5	0.10 ***	833
			Mean	824
0.048 **				

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* Volume of electrolyte 10 ml. Galvanometer sensitivity for fraction 1 : 300; for petroleum 1 : 50.

** Sulfur concentration of crude before dilution with benzene.

*** Values of the diffusion current are given here.

of sulfur in crudes, because the latter did not dissolve readily in this supporting electrolyte. Test crudes were therefore dissolved beforehand in four times their volume of benzene. The relation between wave heights and sulfur concentration in crudes is expressed by the equation $i_d = 824$ c (4) in which, in contrast to the equations (1-3), i_d is equal to the value of the diffusion current. This is explained by the fact that during polarographic determinations of sulfur in crudes, we did not observe minima on the polarograms.

Polarographic curves of some samples of Tuimazinsky crudes and also of samples of Tuimazinsky crudes to which sulfur had been added, are shown in Fig. 3. A consideration of Fig. 3 shows that on Curves 2 and 4 there is a clearly defined polarographic wave for the reduction of sulfur. The other curves fuse into the supporting electrolyte curve. Polarograms show that elemental sulfur is only present in sample 3. The elemental sulfur content of this crude, calculated by means of equation (4), taking into account its dilution with benzene, amounted to 0.01 wt.%. Since the crudes from many fields contain, in addition to elemental sulfur, mercaptans, disulfides, and sulfides, it was of interest to establish the effect of these latter on polarographic determination of elemental sulfur (Table 2).

Consideration of the results given in Table 2 show that under our experimental conditions, mercaptans distort the polarographic curve, i.e., their presence interferes with the polarographic determination of sulfur; the aliphatic sulfides and disulfides which we studied did not distort the polarographic waves for elemental sulfur, and consequently do not intefere with determination of the latter.

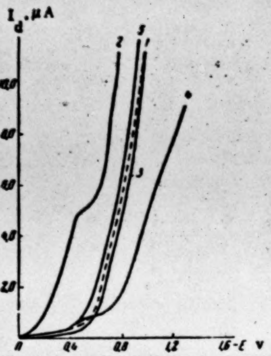

Fig. 3. Polarograms for some Tuimazinsky crudes dissolved in benzene: 1) Curve for the supporting electrolyte; 2) synthetic solution of elemental sulfur in crude (sample 1); 3) crude – sample 2; 4) crude – sample 3; 5) crude – sample 1.

DISCUSSION OF RESULTS

Comparison of the proportionality coefficients in equations (1-3) show that their value decreases with increasing molecular weight of the fractions. Since the proportionality constant enters into the diffusion coefficient, it is possible that the decrease in the value of the proportionality coefficient can be explained by a decrease in the rate of diffusion of sulfur molecules. Change in diffusion rate, all other conditions being the same, can be related to either changes in viscosity of the medium, or to changes in the molecular weight of the diffusing elemental sulfur. The probability of the first being true is very small, since the amount of test material added to the supporting electrolyte is too small, so that the viscosity hardly changes at all.

Special tests showed that the amount of test fraction introduced into the electrolytic cell (Table 3) has no effect on the value of the proportionality coefficient, and consequently, so it would seem, on the diffusion rate. The second hypothesis advanced above is more probable, viz. change in molecular weight of elemental sulfur, with changes in the hydrocarbon composition of the petroleum fraction. This hypothesis however will have to be the subject of a special study.

TABLE 2

Effect of Certain Organic Sulfur Compounds on the Polarographic Determination of Elemental Sulfur Dissolved in 175-200° Fractions

Concentration of sulfur in the original solution, in wt.%	Organic sulfur compound added to the test solution	Concentration of organic sulfur compound in original solution in wt.%	Wave height for elemental sulfur in mm		
			before addition of organic sulfur compound	after addition of organic sulfur compound	after removal of mercaptan
0.085	n-Heptyl mercaptan	0.025	6	No wave observed	6
0.170	Thiophenol	0.095	13		13.5
0.170	n-Dibutylsulfide	0.180	13	13	—
0.170	n-Dibutyldisulfide	0.025	13	13	—

TABLE 3

Effect of the Amount of Test Solution Introduced on the Value of K*

Volume of fraction added to the electrolyte, in ml	Volume of K
0.1	173
0.05	173
0.025	173

In view of the fact that the value of K depends on the composition of the test fraction, calibration of the apparatus must be carried out under comparable conditions.

Mercaptans should be removed beforehand by shaking the test fraction with an aqueous solution of silver nitrate. Dissolved hydrogen sulfide will be removed at the same time.

SUMMARY

1. A polarographic method has been developed for determining elemental sulfur in ligroins, kerosenes,

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* The concentration of elemental sulfur dissolved in the 250-275° fraction, is equal to 0.420 wt.%.

and solar petroleum fractions, as well as in crudes. The sensitivity of the method, depending on the material being analyzed, varies from 0.002 to 0.008 wt.%.

2. It has been shown that the proportionality coefficient in the equation $i_d = Kc$, which expresses the relation between i_d and concentration of elemental sulfur, is lower, the higher the temperature range of the test fraction.

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POTENTIOMETRIC METHODS OF STUDYING HIGH MOLECULAR WEIGHT PETROLEUM COMPOUNDS

3. POTENTIOMETRIC DETERMINATION OF PEROXIDE NUMBERS*

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Potentiometric methods of titration have essential advantages over indicator methods for studying the chemical nature of strongly colored organic compounds and their mixtures. It has been shown [1], that by means of the potentiometric method it is possible to get satisfactory results for determination of saponification numbers and acid numbers, in such complex and dark colored mixtures of organic compounds as petroleum resins.

In the present article it is demonstrated that it is also possible to use this technique successfully for determining peroxide numbers in strongly colored petroleum products. The most useful and reliable methods for the quantitative determination of active oxygen in organic peroxides are the stannometric and iodometric methods [2]. All the same, the stannometric method only gives satisfactory results during quantitative determination of active oxygen in hydroperoxides; when this method is used for analysis of dialkyl peroxides, low results are obtained (lower than by the iodometric method). The iodometric method is not applicable to the analysis of peroxides or mixtures containing them, if the peroxides contain multiple bonds. In such cases, the iodine which is liberated on reaction of sodium iodide with peroxides, is partly or completely used up for reaction with the multiple bonds.

A method has been described [3], for determination of peroxides in the presence of mono-olefinic hydrocarbons by titration until complete disappearance of the iodine color. This iodometric method is not applicable to the quantitative determination of peroxides in solution of colored materials, e.g., petroleum products containing resins.

The work described here was undertaken with the object of studying the conditions under which it would be possible to apply a potentiometric method for determining the amount of iodine liberated on interaction of sodium iodide with peroxides. In the course of the work we had in mind the solution of a limited problem, viz. to establish the possibility of determining the equivalence point in solutions of a strongly colored product (petroleum resins).

Experimental Procedure

An aliquot of test material was dissolved in a mixture consisting of 20 ml absolute isopropanol and 2 ml glacial acetic acid, 10 ml of a saturated solution of NaI in absolute isopropanol was then added to the solution, and the whole boiled on a bath for 5 minutes, after which 5 ml of water was added to the solution, and the final solution immediately titrated potentiometrically with 0.1 N thiosulfate, using an "LP-5" tube potentiometer. The indicator electrode was a platinum electrode whose potential was determined by the ratio of the concentrations of ionic and molecular iodine. The reference electrode was a saturated calomel electrode; any other electrode with a constant potential can however, be used.

The system used was therefore as follows:

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* Part 2: J. Anal. Chem. 11, 731 (1956).

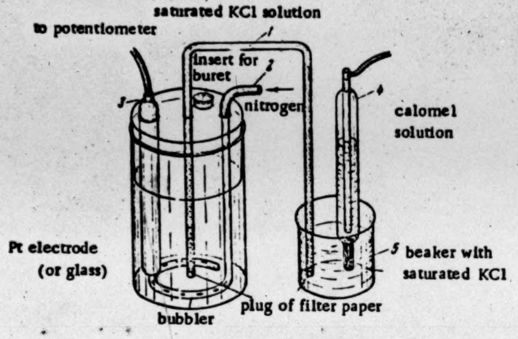

Fig. 1. General appearance of titration cell: 1) syphon with saturated KCl solution; 2) bubbler; 3) platinum electrode; 4) calomel electrode; 5) beaker with saturated solution of KCl.

Pt	j_1/j_2 In solution in isopropanol plus water	Saturated solution of KCl in water	$Hg_2Cl_2 \mid Hg$

Titration was carried out as follows.

The platinum electrode and syphon containing the KCl solution which connects the platinum half-element to the calomel electrode, were placed in the titration vessel, and thiosulfate solution slowly added while the solution was continuously agitated by passing nitrogen through a bubbler. (Fig. 1). By carrying out titration in a nitrogen atmosphere, the possibility of further oxidation by atmospheric oxygen was eliminated. At the same time, the passage of a stream of nitrogen through the solution, which ensures adequate agitation, does away with the necessity of using a stirrer.

TABLE 1

Determination of Active Oxygen in Organic Peroxides in the Presence of Resin,[*] by Potentiometric Titration

Benzene peroxide					1,1-Diphenylethane hydroperoxide				
sample weight		amount used for titration		%	sample weight		amount used for titration		%
peroxide	resin	calculated	found		hydroperoxide	resin	calculated	found	
0.0182	0.0802	1.94	1,97	101.8	0,0255	0.2560	3.15	3,16	100,2
0.01197	0.1020	1.62	1.60	98.9	0.0148	0,1112	1.83	1.82	99.4
0.0200	0.1004	2.28	2,28	100.0	0.0490	0.1346	6.05	6.00	99,2
0,0110	0.1133	1.98	1,96	99,0	0,0254	0.1848	3.14	3.08	97.5
0.0197	0.1614	2,16	2.20	101,8	0.0188	1.2614	2.32	2.33	99.6
0.0229	0,1001	2.00	1,98	99.3	0,0155	0,1416	1.91	1.91	100.0
0.0255	0,2800	2,77	2.77	100.0	0.0300	0.1002	3,7	3,8	102.8

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[*] Resin from Ilsky Petroleum, CCl_4 fraction insoluble in phenol.

TABLE 2

Comparison of the Results of Potentiometric and Indicator Methods for Determination of Active Oxygen in Organic Peroxides

Indicator method								Potentiometric method							
benzene peroxide				1, 1-Diphenylethane hydroperoxide				benzene peroxide				1, 1-Diphenylethane hydroperoxide			
sample weight	amount used for titration		%	sample weight	amount used for titration		%	sample weight	amount used for titration		%	sample weight	amount used for titration		%
	calcu-lated	found			calcu-lated	found			calcu-lated	found			calcu-lated	found	
0.1247	13.54	13.22	98.2	0.1198	14.70	14.82	101.0	0.0282	3.06	3.08	100.6	0.0447	5.50	5.44	98.9
0.0810	8.79	8.6	98.0	0.0900	11.10	11.38	102.5	0.0201	2.18	2.17	99.6	0.0429	5.29	5.20	98.2
0.0707	7.63	7.82	102.5	0.0613	8.16	8.16	100.0	0.0856	1.4	1.15	101.0	0.0255	3.15	3.16	100.2
0.0613	6.65	6.58	99.0	0.0305	3.78	3.78	100.0	0.0324	3.52	3.44	97.5	0.0203	2.52	2.55	101.2
0.0500	5.43	5.45	100.5	0.0397	4.92	5.00	101.8	0.0366	3.92	3.88	99.0	0.0242	2.9	2.83	97.5
0.0424	4.60	4.62	100.4	0.0484	5.97	6.07	101.8	0.0273	2.97	2.97	100.0	0.0204	2.52	2.50	99.5
0.0769	8.34	8.34	100.0	0.0593	7.32	7.28	99.5	0.0367	3.99	4.02	100.8	0.0242	2.96	3.02	101.6
0.0196	2.14	2.15	100.4	0.0828	8.02	8.00	99.8	0.0419	4.56	4.48	98.2	0.0240	2.96	3.00	101.2
0.00488	5.30	5.34	100.6	0.0702	8.68	8.70	100.2	0.0418	4.04	4.02	99.4	0.0220	2.72	2.64	97.0
0.0601	6.52	6.57	100.8	0.0501	6.19	6.20	100.1	0.0385	4.20	4.25	101.0	0.0188	2.32	2.32	100.0

In those cases where contact with air does not lead to complications, titration can be carried out in a closed vessel with the usual stirrer. The vessel should be kept closed in order to avoid loss of iodine by volatilization, though usually the amount of volatilized iodine is always less than experimental error. Up to the equivalence point, the potential of the indicator electrode, and therefore the E. M. F., changes very little; at the equivalence point the potential changes very sharply. The potential change brought about by 1 % thiosulfate on the total amount of the latter in the titration vessel, at the equivalence point, amounts to approximately 70-100 millivolts. In this circuit the potential of the indicator electrode at the equivalence point is approximately equal to the potential of the saturated calomel electrode, i.e., the E. M. F. is almost zero (± 10 millivolts). Accordingly, titration can be carried out up to the jump or to the point at which the E. M. F. is approximately zero. Titration up to the jump has the advantage that in this case, there is no need for a very accurate potentiometer, or need to check the electrodes. For rapid determination (by titrating up to the potential jump), as long as an accuracy of 1 % is sufficient, there is no need to construct a titration curve.

The method described has been checked both on pure benzene peroxide and 1,1-diphenylethane hydroperoxide, as well as on benzene peroxide and 1,1-diphenylethane hydroperoxide to solutions of which petroleum resins had been added.

The experimental results obtained during potentiometric titration of solutions of these materials are given in Table 1. These results agree with those obtained by means of an indicator based on a widely used iodometric method (Table 2).

SUMMARY

A method has been suggested for potentiometric determination of peroxide numbers in solutions of petroleum resins, in which a smooth platinum electrode is used.

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A COLORIMETRIC METHOD FOR THE DETERMINATION OF CERTAIN AROMATIC AMINES AND THEIR DERIVATIVES

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In a previous article by one of the authors [1], a description was given of a new colorimetric method of determining certain phenols and naphthols, which was based on their color reactions with chloramine. Since, according to published data [2], chloramine gives colors not only with phenols, but with aromatic amines as well, we tried to extend this method to cover determination of the latter.

Chloramine T (the sodium salt of p-toluenesulfochloramide) gives an orange-yellow, or rose color, in aqueous solutions with most aromatic amines; we used this reaction for their colorimetric determination. Determinations were carried out as follows: an aliquot of test material, containing from 0.05 to 0.2 g of amine or its salt, was dissolved in distilled water in a 1 liter standard flask, 50 ml of a 10% aqueous solution of chloramine T was then added, and the volume made up to the mark with water. At the same time a standard solution was made up in exactly the same way from the appropriate chemically pure amine. After standing for 2 hours, the colors of the solutions were compared by means of a Duboscq colorimeter.

Chloramine B can be used instead of chloramine T (the former is the corresponding benzene derivative); it gives, as our experiments showed [3], identical results with those obtained with chloramine T for oxidation of organic materials.

Completely satisfactory results were obtained during the colorimetric determination of aniline, o-, m-, and p-toluidines, p-phenylenediamine and p-amidophenol (Table 1).

TABLE 1

Determination of Certain Aromatic Amines

Amine	Amount taken in g	Amount found in g	Difference in g
Aniline sulfate	0.058, 0.221	0.055, 0.225	−0.003, +0.004
o-toluidine	0.120, 0.200	0.121, 0.213	−0.001, +0.013
m-toluidine	0.111, 0.219	0.115, 0.221	−0.001, +0.004
p-toluidine hydrochloride	0.057, 0.200	0.055, 0.199	−0.003, −0.001
p-phenylenediamine sulfate	0.050, 0.226	0.055, 0.231	−0.002, +0.005
p-aminophenol	0.180, 0.379	0.173, 0.390	−0.020, −0.007

By making appropriate modifications, the method can also be used for determination of some derivatives of aromatic amines. We give here only the method for determining important pharmaceutical products − Phenacetin (acetyl-p-phenetidine) and pyramidone (4-dimethyl-amino-1-phenyl-2,3-dimethylpyrazolone).

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* Deceased.

Hitherto there has been no satisfactory method for determining phenacetin [4]. The State Pharmacopeia of the USSR (VIII Edition) does not give methods for determining phenacetin quantitatively, nor does P. L. Senov's textbook on pharmaceutical chemistry. The method recommended by Perelman and Brodsky [5], cannot give satisfactory results. Vaisman's method [6], which is based on hydrolysis of phenacetin and titration of liberated acetic acid with alkali, is long, and is not suitable in the presence of many other preparations, e.g., aspirin which is often used in conjunction with phenacetin.

On the basis of a color reaction with chloramine, we have developed a simple method for determining phenacetin, which can also be used in the presence of other compounds which normally accompany it in medicinal preparation.

Determination was carried out as follows: an aliquot of test material containing from 0.1 to 0.3 g of phenacetin, was dissolved in 100 ml 90% ethanol, where necessary (e.g., during tablet analysis) the solution was filtered; 25 ml of a 5% aqueous solution of chloramine was then added and the mixture heated to the boil, at which an intense yellow color developed. On cooling, the solution was quantitatively transferred to a 250 ml standard flask and the volume made up to the mark with 90% ethanol. The solution obtained was then colorometrically compared with a solution prepared in the same way from 0.2 g of pure phenacetin. The method gave quite satisfactory results (Table 2), while the presence of such compounds as aspirin, caffeine, methylcaffeine and sodium salicylate, which often accompany phenacetin, did not interfere with the determination of the latter. The considerably more poisonous, free phenetidine, which can be present in phenacetin as an impurity, gives a similar color reaction with chloramine.

TABLE 2

Determination of Phenacetin

Phenacetin taken in g	Amount added in g of	Phenacetin found in g	Difference in g
0.100, 0.300		0.098, 0.295	—0.006, —0.002
0.250	Caffeine 0.05	0.240, 0.245	—0.005, —0.010
0.250	Methylcaffeine 0.25	0.243, 0.246	—0.006, —0.010
0.250	Aspirin 0.25	0.240, 0.245	—0.005, —0.010
0.300	Sodium salicylate 0.300	0.290, 0.302	—0.010, +0.002

Pyramidone, which reacts in the same way as phenacetin with chloramine, interferes. The yellow color which is formed on interaction of phenacetin with chloramine, disappears on addition of a few drops of concentrated hydrochloric acid, while the color formed between pyramidone and chloramine stays. We have based a method for colorimetric determination of pyramidone on this fact. This method has the advantage over the method recommended in the eighth edition of the USSR Pharmacopeia, which is based on titration with hydrochloric acid, in that this latter method does not take into account the fact that other compounds of a basic character can be titrated as well; the same applies to the method of Schulek and Menyart [7], which is based on oxidation of pyramidone with 0.1 M permanganate, followed by iodometric determination of excess permanganate; in this case other materials which can be oxidized also react with permanganate.

Pyramidone was determined as follows: an aliquot of test material, containing 0.1-0.3 g of pyramidone was dissolved in 200 ml 90% ethanol, the solution was filtered where necessary, and 25 ml of a 5% aqueous solution of chloramine added, the mixture was heated to the boil and then acidified with 2-3 drops of concentrated hydrochloric acid; on cooling, the solution was quantitatively transferred to a 250 ml standard flask and made up to the mark with 90% alcohol. A standard solution was made up in exactly the same way from 0.2 g of pure pyramidone. The solutions were then compared colorimetrically using a Duboscq colorimeter. A determination takes about half an hour.

The method gives satisfactory results (Table 3); phenacetin, caffeine, veronal, aspirin, and codeine do not interfere.

TABLE 3

Determination of Pyramidone

Pyramidone taken in g	Amount added in g of	Pyramidone found in g	Difference in g
0.100, 0.300	—	0.098, 0.292	−0.002, −0.008
0.250	Phenacetin 0.250	0.241, 0.260	−0.008, +0.010
0.300	Aspirin 0.300	0.292, 0.304	±0.000, −0.008
0.300	Veronal 0.100	0.292, 0.297	−0.003, −0.012
0.300	Caffeine 0.100	0.288, 0.292	−0.008, −0.012
0.300	Codeine 0.015	0.284, 0.291	−0.016, −0.009

SUMMARY

1. A simple method has been developed for the colorimetric determination of some aromatic amines (aniline, o-, m-, and p-toluidines, p-phenylenediamine, p-amidophenol) based on their color reaction with chloramine.

2. This method has been modified to allow determination of phenacetin in the presence of aspirin, caffeine, methylcaffeine, and sodium salicylate, and also of pyramidone in the presence of phenacetin, caffeine, veronal, aspirin, and codeine.

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AMPEROMETRIC TITRATION OF GOLD WITH HYDROQUINONE

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Development of methods for the determination of gold in the presence of tellurium, selenium, and palladium is of great practical interest, since these elements are sometimes found together in natural ores and their processed products; moreover, they accumulate in waste from sulfuric acid production by the lead chamber process, and in anode sludge during electrolysis.

A description is given in the present article of an amperometric method of determining gold in the presence of tellurium, selenium, and palladium using a rotating platinum microanode.

The set-up used for amperometric titration had a galvanometer with a sensitivity of 1.4×10^{-9} A (from 1/20 to 1/100) fitted with a shunt.

The rotating platinum micro-electrode was a platinum wire 0.8 mm in diameter and 1 mm long, fused into a glass tube fitted onto the shaft of a motor. The electrode was rotated by means of a three phase current motor at the rate of 800-900 revolutions/minute. A saturated calomel electrode was used as the reference electrode. Amperometric titration of potassium chloroaurate in a supporting electrolyte of 2N H_2SO_4 was carried out in a thermostat at 60 ± 1°, under which conditions the best reproducibility of results was obtained. At this temperature, gold is rapidly reduced by hydroquinone; at lower temperatures, the reaction is slow and such temperatures are not suitable for carrying out the titration.

The hydroquinone was purified by sublimation. Hydroquinone gives a well defined limiting current [1]. The current-voltage curve for hydroquinone is shown in Fig. 1.

TABLE 1

Au concentration in M/liter	Au taken in mg	Au found in mg	Error in %
$9.8 \cdot 10^{-2}$	19.5	20.2	3.5
$7.9 \cdot 10^{-2}$	15.6	15.8	1.3
$5.9 \cdot 10^{-2}$	11.7	11.8	0.8
$3.9 \cdot 10^{-2}$	7.8	7.9	1.3
$2.9 \cdot 10^{-2}$	5.8	6.1	5.2
$1.9 \cdot 10^{-2}$	3.9	4.2	7.7
$1.8 \cdot 10^{-2}$	3.7	4.0	8.1
$8.1 \cdot 10^{-3}$	1.6	1.6	—
$6.1 \cdot 10^{-3}$	1.2	1.27	6.6
$5.9 \cdot 10^{-3}$	1.17	1.16	1.0
$4 \cdot 10^{-3}$	0.78	0.83	6.4
$2 \cdot 10^{-3}$	0.39	0.38	3.0
$9.5 \cdot 10^{-4}$	0.19	0.17	10.0

TABLE 2

Au taken in mg	Added in mg			Au found in mg	Error in %
	selenium	tellurium	palladium		
3.89	—	4.0	—	4.12	5.9
7.79	—	4.0	—	7.70	1.2
3.90	1.0	—	—	4.08	4.8
7.79	1.0	—	—	8.19	5.1
3.90	—	—	2.4	3.85	1.3
7.79	—	—	1.2	7.38	5.2
7.79	—	—	2.4	7.16	9.4
1.56	3.0	6.0	1.2	1.46	6.5
1.94	1.0	2.0	1.2	1.93	0.5
3.12	3.0	6.0	1.2	3.01	3.5
3.89	1.0	2.0	1.2	3.88	0.5
3.73	0.5	1.0	1.2	3.70	0.8
2.99	3.0	6.0	1,2	2.90	3.0
5,97	6.0	1.2	1.2	5.76	3.5
7.46	1.0	2.0	1.2	7.44	0,3

Gold was determined by means of hydroquinone by adding 200 ml of 2N H_2SO_4 to a known volume of a potassium chloroaurate solution in the electrolytic cell, and titration carried out with hydroquinone at a potential of 1.0 v with respect to the saturated calomel electrode, using the platinum micro-electrode. The value of the limiting current was measured after each addition of hydroquinone solution. The limiting current was established very rapidly during titration. Titration curves are shown in Fig. 2.

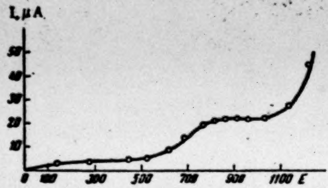

Fig. 1. Polarogram for hydroquinone in a supporting electrolyte of 2 N H_2SO_4.

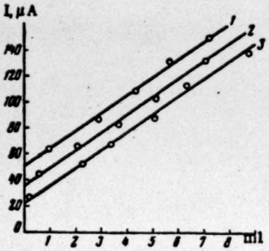

Fig. 3. Amperometric titration curve for selenium, tellurium, and palladium with hydroquinone at φ = 1.0 v in a supporting electrolyte of 2N H_2SO_4: 1) determination of selenium; 2) determination of tellurium 3) determination of palladium.

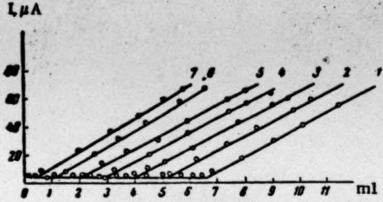

Fig. 2. Amperometric titration curves of gold: 1) titration of 22.9 mg of Au without any additives; 2) titration of 17.9 mg Au in the presence of tellurium; 3) titration of 14.0 mg Au in the presence of selenium; 4) titration of 10.3 mg Au in the presence of palladium; 5) titration of 6.9 mg Au in the presence of selenium, tellurium, and palladium; 6) determination of 4.2 mg Au in anode slurry; 7) determination of 1.7 mg Au in an ore.

Table 1 contains the results of amperometric titrations of various amounts of gold in pure solutions. The results given are the means of 5-7 determinations.

A consideration of these results shows that in fairly dilute solutions (from 10^{-2} M/liter to 10^{-4} M/liter or to 0.2 mg/liter Au) it is possible to determine gold amperometrically with an accuracy of 1-10% at 60°.

Table 2 contains the results for amperometric determination of gold in the presence of selenium, tellurium, and palladium.

These results are also the means of 5-7 determinations.

As special experiments showed, (Figs. 2 and 3, Curve 5), selenites, tellurites, and the ion of divalent palladium, are not oxodized on a platinum anode at a potential up to 1.1 v, and are not reduced by hydroquinone. The error for determination of 1.5 to 20.0 mg of gold in 1 liter, on an average, amounted to 1-9.5%.

Table 3 contains the results for determination of gold in ores and anode sludges after electrolysis.

Amperometric determination of gold with hydroquinone in this case was carried out after decomposition of the Ore* or sludge.

The amperometric method of determining gold in ores and sludges gives fully satisfactory results, which agree with those obtained by extraction of gold by mercury from ores, and by oxalic acid from sludges respectively. We should like to thank Yu. V. Morachevsky for valuable advice and help.

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* The precipitate obtained after decomposition of the ores with concentrated sulfuric acid, was carefully calcined; it was then dissolved in aqua-regia. Nitric acid was removed by repeated addition of HCl while the solution was being boiled. The solution of gold chloride prepared in this way was then analyzed amperometrically.

TABLE 3

Determination of Au in 100 g of ore*	Determination of Au in 2.5 g of sludge**
found in mg	found in mg
2.12 2.13 1.80 1.70	4.32 4.43 4.45 4.04 4.68 4.59
Mean value 1.94	Mean value 4.42

* The amount of Au found in this ore by extraction with mercury was 1.6 mg.

** The amount of Au found in this sludge by precipitation of Au with oxalic acid was 4.48 mg.

SUMMARY

It has been demonstrated that it is possible to determine gold by amperometric titration with hydroquinone in the presence of selenium, tellurium, and palladium, and that amperometric titration can also be used for determining gold in ores and sludges.

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BRIEF COMMUNICATIONS

A COLOR REACTION FOR HYDRAZINE

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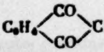
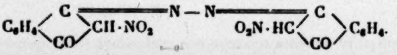
We showed recently [1], that hydrazine reacts in acid media with 2-nitroindanindandione-1,3(I) to form an orange-red azine (II). Test experiments showed that the orange color of the solution appears at quite high dilutions of the hydrazone salts. Since there are hardly any good color reactions for hydrazine [2], it seemed a good idea to develop a new color reaction for this compound.



(I)



(II)

When nitroindandione is added to an aqueous solution of hydrazine hydrochloride, and the mixture boiled, the solution will, depending on the concentration of the hydrazine salt, rapidly acquire an orange or orange-red color, while at high hydrazine concentrations, particularly on cooling, an orange-red precipitate of the azine of nitroindandione will settle out. A similar reaction occurs with hydrazine sulfate. Excess nitroindandione favors the reaction. Although nitroindandione is itself a strong acid, nevertheless the presence of a mineral acid speeds up development of the color and makes the reaction somewhat more sensitive. For average concentrations of hydrazine, it is sufficient to heat for 2-3 minutes; at very low concentrations it is necessary to prolong this heating to 10 minutes. Since during such prolonged heating the liquid becomes concentrated as a result of evaporation, we placed the test tubes in a beaker with boiling water and observed the gradual change in color. We also treated test tubes containing aqueous solutions of nitroindandione of the same concentration as the hydrazine salts in the same way, and found no interference. The solution of nitroindandione, which is yellow, acquires a more or less clearly defined orange color in the presence of hydrazine. The limiting dilution at which it is still possible to detect an orange color in the case of hydrazine hydrochloride is 1 : 50,000, or, in terms of free hydrazine, approximately 1 : 100,000.

Hydrazine can be detected as follows. To 1-3 ml of the aqueous solution of hydrazine is added 2-3 drops of concentrated hydrochloric acid, and crysalline nitroindandione in such amount that a solution containing at least 6-7% of nitroindandione is obtained (excess of the latter does not interfere and, in fact, increases the sensitivity). The mixture is gently boiled. After a few minutes an orange color should develop; at high hydrazine concentrations this color changes to orange-red. In the latter event, on standing, an orange-red precipitate of nitroindandione azine usually settles out.

One of the drawbacks of many color reactions for hydrazine is the fact that hydroxylamine usually gives the same reaction. Since it is known that nitroindandione in acid media gives a yellow oxime with hydroxylamine [3], one would expect it not to interfere with detection of hydrazine. This is actually the case. Since the oxime of nitroindandione is only slightly soluble, it is precipitated; when hydrazine is present, this precipitate of the oxime acquires an orange shade; the liquid above the precipitate is orange. The following facts were established experimentally.

0.5 g of hydroxylamine hydrochloride was dissolved in 5 ml of hydrazine hydrochloride at a dilution of the latter of 1 : 10,000. The ratio of the salts in this solution was accordingly 1 : 1,000, to 2 ml of this solution was added 2-3 drops of concentrated hydrochloric acid and 0.2-0.3 g of nitroindandione On boiling, complete solution was attained initially ;subsequently, nitroindandione oxime separated out. This precipitate and the liquid rapidly acquired and orange color. On standing, this color became stronger.

On the assumption that all the hydroxylamine taken reacts with the nitroindandione to form the oxime of the latter, while one still has excess of the nitroindandione to react with hydrazine, it should have been necessary, in the experiment just described, to take about 0.7 g of nitroindandione Test showed, however, that it is sufficient to take the amount indicated above (viz. 0.2-0.3 g). It follows from this that formation of the oxime and azine respectively, proceeds in parallel. When the pure oxime of nitroindandione is heated with a solution of 1 : 1,000 of hydrazine hydrochloride, the oxime slowly acquires an orange shade. This means that the oxime can be partially converted into the azine by the action of an hydrazine salt. Addition of a few drops of hydrochloric acid speeds up this process.

The experiment was repeated with a solution of hydrazine hydrochloride at a dilution of 1 : 50,000 to which was added 0.5 g of hydroxylamine hydrochloride. The ratio of the salts in solution was 1 : 5,000. On boiling for a slightly longer time, an orange color which was still quite discernible was obtained.

Thus hydrazine can still be detected in the presence of 5,000 times its amount of hydroxylamine, in solution by means of nitroindandione.

Nitroindandione was prepared by nitrating indandione [4].

SUMMARY

A new color reaction has been developed for hydrazine. An aqueous solution of hydrazine, acidified with concentrated hydrochloric acid, is boiled with excess 2-nitroindandione-1,3. The azine of nitroindandione which colors the solution orange is formed. At high hydrazine concentrations, an orange-colored precipitate of this azine settles out on standing. The limiting dilution of hydrazine at which this orange color can still be observed is 1 : 100,000.

Under the same conditions, hydroxylamine only gives a yellow-colored oxime which is sparingly soluble, and is accordingly precipitated; this precipitate does not interfere with the development of an orange color for hydrazine, and it is possible to determine hydrazine in the presence of 5,000 times its amount of hydroxylamine in solution.

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[2] L. M. Kulberg and A. I. Cherkesov, J. Anal. Chem. 6, 364 (1951).

[3] G. Vanag and V. Vitol, Bull. Acad. Sci. Latvian SSR, No. 7, (60) 107 (1952).

[4] G. Vanag, Nitroindandione (Acad. Sci. Latvian SSR Press, Riga, 1954) p. 11.

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* T.p. = C. B. Translation pagination.

CHRONICLE

A NEW JOURNAL ON ANALYTICAL CHEMISTRY

In August 1956 the first number of a new journal on analytical chemistry made in its appearance in Poland (Warsaw); it is called "Chemia Analityczna" and is the organ of the newly created Polish Commission on Analytical Chemistry which is part of the Chemical Sciences Section of the Polish Academy of Science. The editor is V. Kemula, while the sub-editors are M. Makhailsky and E. Minchevsky.

The journal will be published quarterly in an edition of 3,000. The aim of the journal will be to give as complete information as possible on acievements of Polish analytical chemists in analysis and the publication of original papers describing work carried out in scientific-research institutes and educational establishments.

The first number of the journal included a number of articles devoted to the analysis of organic compounds, and also to questions in the field of emission spectrographic analysis. The journal includes a section entitled "Laboratory Notes." A bibliography is given of books and journal articles published by Polish Scientists in other journals.

All published review and original papers have a summary in English and Russian.

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QUESTIONS RELATING TO THE ANALYTICAL CONTROL OF PRODUCTION AT A CONFERENCE ON THE CHEMISTRY AND TECHNOLOGY OF GALLIUM, INDIUM AND THALLIUM

(Held at Kiev on 28-30 June 1956)

Reports were read at this conference dealing with improvement and development of new methods for the quantitative determination of gallium, indium, and thallium in ores, concentrates, and products obtained during their processing (spectrographic, photometric, polarographic methods of analysis), and also to the development of determining impurities (other metals) in gallium, indium, and thallium. In addition, questions relating to the study of complex formation by gallium, indium, and thallium were also considered, as well as the the study of hydrolysis of these metals.

A. K. Babko, A. I. Volkova and N. N. Zakharova gave their results on work they had carried out to check the efficiency of various methods for isolating indium, and the extent of its separation from other elements, using the methods of radioisotopes and spectrographic analysis, respectively. They found that the most rapid methods are precipitation of indium with pyridine, and extraction of indium bromide with ether. A method has been developed for determining micro amounts of lead. 3-5 γ of lead can be determined in 0.2 g of metallic indium by means of dithizone. It is recommended that arsenic (5-10 γ) be determined nephelometrically after its reduction to the elemental stage and subsequent flotation with an organic solvent.

N. T. Voskresenskaya (Moscow University) read a paper on the photometric determination of thallium by means of Brilliant Green. This work was published in J. Anal. Chem. 11, 585 (1956).

The report read by A. I. Zebrova and M. T. Kozlovsky (Kazakh State University) was devoted to the polarographic determination of thallium in the presence of Cu, Pb, Cd, Sb, Se, Tl, Bi, and Fe in certain industrial solutions; they used a mixed supporting electrolyte.

The report by V. A. Tsimmergakl and T. D. Kazakovtseva was devoted to polarographic determination of zinc, cadmium, and lead in metallic indium.

The report of T. E. Arefyeva and L. B. Ginsburg (Gintsvetmet)* touched on methods for the polarographic and photometric determination of gallium, indium, and thallium in the dust of lead-zinc and copper factories.

V. M. Vladimirova and B. S. Tsyvina (Giredmet)** read a report on an amperometric method for titrating indium with a complexone in concentrates and waste processed material from zinc and tin production. By means of this method it is possible to determine 0.4 mg of indium in a 2 g sample. Photometric determination using the hydroxyquinoline method is recommended for determining smaller amounts.

B. S. Tsyvina and T. V. Cherkashina (Giredmet) devoted their paper to a complexometric (with Complexone III) method of determining gallium at a pH of 7-9 using Eriochrome Black T as indicator. The accuracy of the method for a content of 1 mg is 1%, at higher contents the accuracy is 0.1-0.3% (relative). The method has been developed so that it can be used for raw materials, intermediate enrichment products and gallium concentrates.

A photometric method with hydroxyquinoline is used for determination of gallium in wastes. The sensitivity of the method is better than 0.001% for a sample of 1 g.

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* Gintsvedmet = State Institute of nonferrous metals.

** Giredmet = State Scientific Research Institute for Rare Metals.

The report of I. M. Blokh and S. M. Solodovnik (Giredmet) dealt with the spectrographic determination of dispersed elements in raw materials and of impurities in the dispersed elements.

A number of reports were devoted to physicochemical studies of the simple and complex compounds of gallium, indium, and thallium, the hydrolysis of their salts, coprecipitation processes, etc.

I. V. Tananaev read a paper on the ferrocyanides of gallium, indium, and thallium.

The report of D. M. Chizhikov, N. A. Gurovich, and D. M. Denisova (Metallurgical Institute of the Acad. Sci. USSR) touched on the hydrolysis of indium sulfate. The reports of E. N. Deichman were devoted to a study of the formation of indium hydroxide and the separation of the hydroxides of indium and zinc; that of N. V. Akselrud and B. V. Spivakovsky to a study of alkaline solutions of indates; that of A. A. Shokol and L. F. Kozin to a study of the conditions of coprecipitation of indium with ferric hydroxide, and of zinc, cadmium, and copper with indium hydroxide.

The papers by G. S. Savchenko and E. V. Goncharov touched on the composition of the tartrates of gallium in aqueous solutions; that of Ya. A. Fialkova and N. K. Davidenkc was devoted to the complexes formed between gallium and trihydroxyglutaric acid.

The reports evoked considerable interest. In the ensuing discussions a number of critical observations were made, which were directed at further improving scientific-research work.

In the resolutions adopted by the conference, a program was formulated for further studies in the chemistry and technology of gallium, indium, and thallium.

I. A. Sheka

THE USE OF ANALYSIS OF VARIANCE IN EVALUATING EXPERIMENTAL RESULTS

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In a previous article [1], analytical errors were classified, and it was shown that under certain conditions methodological errors can be regarded as random values. On the basis of the central limiting theorem of Lyapunov, conditions were considered under which one would expect normal distribution of analytical errors, and consequently one could employ the criteria t, χ^2, and F. The idea of applying modern mathematical statistics is motivated primarily by the consideration that by means of this method it should be possible to carry out calculations with low random selections, as long as they consist of at least two members. The element of indeterminacy which is introduced during such calculations is taken into account by means of the criteria indicated above; these criteria enable one to evaluate the reality of the existence of the effects being studied and to establish confidence limits for them.

Analysis of variance, which has been developed to a considerable extent by the English statistician Fisher [2], can be widely recommended for the study of analytical errors. This method has been used for many years in biology and agriculture, particularly in England. The use of analysis of variance in agriculture has been briefly considered by V. I. Romanovsky [3]. The use of analysis of variance for studying production processes came considerably later. This side of the question has been dealt with thoroughly in the books of Brownlee [4]* and Khald [5]. A number of articles have appeared recently in foreign literature which have been devoted to the use of analysis of variance in analytical chemistry [6-12].

The aim of analysis of variance is to resolve total dispersion into two factors: the dispersion which is the result of experimental technique (error of reproducibility) and the dispersion which is caused by the factor being studied, with an evaluation of the statistical significance of the latter factor. In cases where many factors operate the dispersions which are the results of each of these factors, and of the interaction of the factors, are evaluated and the signifiance of these dispersions are evaluated, taking into account errors of reproducibility. The fundamental difficulty in analysis of variance is the correct choice of a suitable form of analysis of variance, and interpretation of the results obtained. First of all, let us consider the possibility of using analysis of variance for studying random methodological errors which are determined by the characteristics of the chemical composition of test samples. Let us assume that we have m standards, each of which has been analyzed n times. Then the total error (for a mean of n determinations) can be represented by formula (1):

$$\sigma_{\Sigma} = \sqrt{\frac{\sigma^2_{\text{reproducibility}}}{n} + \sigma^2_{\text{random chemical}} + a^2}. \tag{1}$$

where $\sigma_{\text{reproducibility}}$ – is the error of reproducibility for one analysis, $\sigma_{\text{random chemical}}$ is the random experimental error which is determined by the characteristics of the chemical composition of test material, and a is a constant experimental error which is independent of the composition of test material (a shift in the center of scattering relative to the rated results). In order to determine all three values: $\sigma_{\text{reproducibility}}$, $\sigma_{\text{random chemical}}$, and a, from one series of measurements, we shall compile a special table.

In this table we shall include relative errors, calculated with respect to rated results, while in each column we shall place results for any one test sample,* as shown in Table 1. In this table, the dispersions along the columns are determined by reproducibility errors while the dispersions between columns are determined by the characteristics of the chemical composition of the test samples.

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* See footnote to [4] at end of article.

TABLE 1

	Sample I	Sample II	Test with index m
First determination	x_{11}	x_{21}	x_{m_1}
Second determination	x_{12}	x_{22}	x_{m_2}
n-th determination	x_{1n}	x_{2n}	x_{mn}
Mean	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_m$

For determining $\sigma_{\text{reproducibility}}$ and $\sigma_{\text{random chemical}}$ it should be possible to use well known methods: to determine the dispersion individually for each column, and then to find the mean arithmetic value of these dispersions:

$$\sigma^2_{\text{reproducibility}} = \frac{\sum_{i=1}^{m}\sum_{n=1}^{n}(x_{ih} - \bar{x}_i)^2}{m(h-1)} \qquad (2)$$

Afterwards, one can determine the dispersion of the mean values along the columns with respect to the general mean; this dispersion, obviously, is equal to the sum of two dispersions – a dispersion which is determined by the characteristics of the chemical composition of test samples, and a dispersion which is determined by the reproducibility error, divided by the number of replicates:

$$\frac{\sigma_{\text{reproducibility}}}{n} + \sigma^2_{\text{random chemical}} = \frac{\sum_{i=1}^{m}(\bar{x}_i - \bar{x}_T)^2}{m-1} \qquad (3)$$

In order to simplify calculation, one usually determines the following supplementary sum of squares:

$$S = \Sigma x^2 - \frac{(\Sigma x)^2}{mn},$$

, the sum is taken for all observed values of x.

$$S_I = n\left[\sum_{i=1}^{m}\bar{x}_i^2 - \frac{\left(\sum_{i=1}^{m}\bar{x}_i\right)^2}{m}\right]$$

, the sum is taken for the means along all the columns.

or

$$S_I = \frac{\sum_{i=1}^{m}A_i^2}{n} - \frac{(\Sigma x)^2}{mn}.$$

. A_i. here is the sum of values along the columns.

Then we find

$$\sigma^2_{\text{reproducibility}} = \frac{S - S_I}{m(n-1)},$$

$$\sigma^2_{\text{reproducibility}} + n\sigma^2_{\text{random chemical}} = \frac{S_I}{m-1}.$$

---

* Test samples should not differ very much from each other with respect to the component being analyzed, so that there will be no relation between $\sigma_{\text{reproducibility}}$ and concentration of test component. The absence of such a relationship can be established by means of the ratio of the dispersions $F = \sigma^2_{\text{reproducibility I}} / \sigma^2_{\text{reproducibility II}}$ for samples with extreme values for concentration of test component, by comparing it with tabulated results for values of the F-distribution. If the ratio found for the dispersions at a given level of significance is greater than the appropriate tabulated values, then one must accept the existence of a relation between $\sigma_{\text{reproducibility}}$ and concentration.

In order to determine the significance of $\sigma_{\text{random chemical}}$, one finds the ratio

$$F = \frac{\dfrac{\sigma^2_{\text{reproducibility}}}{n} + \sigma^2_{\text{random chemical}}}{\dfrac{\sigma^2_{\text{reproducibility}}}{n}} = \frac{\sigma^2_{\text{reproducibility}} + n\sigma^2_{\text{random chemical}}}{\sigma^2_{\text{reproducibility}}} \qquad (4)$$

Two values of the degrees of freedom are connected with this ratio: m - 1 for the numerator, and m(n-1) for the denominator. By comparing the values found for the F-ratios with tabulated values for the F-distribution, for the given degrees of freedom, one finds the probability of a random appearance of F, on the assumpation that $\sigma_{\text{random chemical}} = 0$ (the null hypothesis in Fisher's terminology). If this probability is sufficiently small, e.g. ≤ 0.05, it will indicate that the null hypothesis is incorrect; in this case, one can affirm with a definite probability the existence of $\sigma_{\text{random chemical}}$. The constant experimental error is equal to the total mean along the whole table:

$$a = \bar{x}_T = \frac{\bar{x}_1 + \bar{x}_2 + \ldots + \bar{x}_m}{m}. \qquad (5)$$

In the absence of a constant experimental error, the total mean of all the table, made up of relative errors, would be equal to zero.

The reality of the existence of a constant experimental error can only be confirmed when the following condition is fulfilled:

$$a \geq \frac{t\sqrt{\dfrac{\sigma^2_{\text{reproducibility}}}{n} + \sigma^2_{\text{random chemical}}}}{\sqrt{m}}. \qquad (6)$$

where t is given by Student's distribution.

We determined the values of $\sigma_{\text{reproducibility}}$ and $\sigma_{\text{random chemical}}$ for a small number of measurements. The upper possible limit for these errors in the general population from which this random small choice was made is determined by the equations:

$$\begin{aligned} \sigma_{\text{general reproducibility}} &= \frac{\sqrt{m(n-1)}}{\sqrt{\chi^2}}\,\bar{\sigma}_{\text{reproducibility}} \\ \sigma_{\text{random chemical, general}} &= \frac{\sqrt{m}}{\sqrt{\chi^2}}\,\bar{\sigma}_{\text{random chemical}} \end{aligned} \qquad (7)$$

Errors obtained on the basis of the small choice are denoted by dashes. Values of χ^2 were taken from tables, in which had been tabulated values of the χ^2 distribution.

In Table 2 are given results of calculations carried out by the scheme described above during a study of experimental errors in the chemical analysis of slags. A study of experimental errors was carried out on synthetic standards made up from standard samples from the Ural Metals Institute. Insignificant values of a and $\sigma_{\text{random chemical}}$ are given in brackets in the table. A consideration of this table shows that in most cases $\sigma_{\text{random chemical}}$ is significant, and in value it is equal to or even several times greater than the reproducibility error. The constant experimental (methodological) error proved to be significant in three cases only: for the gravimetric determination of SiO_2 and for the simplified method of analyzing Al_2O_3, when SiO_2 was only removed once. When one takes into account that analyses, as a rule, were made up from several replicates, it becomes clear that in most cases the total value of the error is determined by the value of $\sigma_{\text{random chemical}}$. The table shows that it is possible, using analysis of variance, to carry out a differential study of analytical errors even on a comparatively small amount of experimental data by evaluating in the appropriate manner the results obtained.

TABLE 2

Test components	Analytical method	Concentration limits	Number of replicates	Number of samples	Experimental (methodological errors		
					$\sigma_{reproducibility}$	$\sigma_{random\ chemical}$	a
MgO	Gravimetric phosphate	2,7-13,2	4	9	3,2	5,7	(+0,5)
MgO	Volumetric complexometric	1,8-13,2	2	10	5,2	(1,6)	(−,01)
SiO_2	Photocolorimetric	12,4-38,7	6	9	2,8	3,2	(−0,8)
SiO_2	Gravimetric, calculating the SiO_2 in one filtrate without treating the precipitate with HF	12,4-38,7	6	10	1,6	2,6	−2,0
SiO_2	Gravimetric, taking into account the SiO_2 in three filtrates, treatment of precipitate with HF	12,4-38,7	4	12	1,0	1,6	−2,6
MnO	Persulfate – silver	2,2-16,6	4	9	3,3	3,6	(−0,9)
CaO	Volumetric, oxalate	22,2-44,8	2	7	0,8	1,2	(−0,9)
Al_2O_3	Gravimetric, phosphate, one treatment for removal of SiO_2	2,1-5,4	4	9	6,4	8,6	+9,7
Al_2O_3	Gravimetric, phosphate, three treatments for removal of SiO_2	1,5-5,4	3	8	5,6	4,6	(+0,3)
Fe_{total}	Volumetric, iodometric	3,3-28,3	4	7	3,0	(1,4)	(−0,6)
Fe_{total}	Volumetric, dichromate	3,5-29,3	2	8	1,1	1,6	(+0,2)

Note: Values of no significance are given in brackets.

It must be emphasized that analysis of variance of errors is only possible in those cases where $\sigma_{\text{reproducibility}}$ will be determined from those measurements which serve for determination of experimental (methododological) errors. The values of $\sigma_{\text{reproducibility}}$ at our disposal for slag analysis, which were obtained for series analysis during the treatment of analytical records, in several cases were double and even more than double the results given in Table 2; this is to be expected since the conditions for series analyses and research work differ essentially from one another.

Analysis of variance can also be applied for determining σ_T of an error, which is determined by noncontrolled changes in conditions of work with time. Experiments are conducted so that one or several test samples are analyzed after a large time interval. Analytical results for each sample are registered as shown in Table 1; in each column is written the result of replicate determinations of this sample carried out at some one particular time. Dispersion along the columns will again be determined by $\sigma_{\text{reproducibility}}$ and dispersion between columns by σ_T.

TABLE 3

Photocolorimeter	Galvanometer sensitivity	Solutions					
		Blue		Yellow		Red	
		$\sigma_{\text{reproducibility}}$	σ_T %C	$\sigma_{\text{reproducibility}}$	σ_T %C	$\sigma_{\text{reproducibility}}$	σ_T %C
EK-M	$0.3 \cdot 10^{-7}$	0.36	1.5	0.29	1.7	0.13	1.70
EK	$1.7 \cdot 10^{-8}$	0.57	2.0	0.90	4.3	0.40	2.24

Table 3 contains the results of calculations carried out by the method of analysis of variance during the study of instrumental errors of photocolorimeters. Errors are expressed in percentage concentration. The error σ_T proved to be significant in all cases, and on an average it was five times the reproducibility error.

We used analysis of variance for studying the stability of calibration curves with time for spectrographic analysis [13]. In this instance, by means of mathematical analysis, the total error was resolved into three factors: reproducibility error, an error connected with slow fluctuations in excitation temperature which was observed only after carrying out observations over a long period and, finally, an error connected with local changes in contrast factor, determined by development effects.

Analysis of variance can be used for studying the heterogeneity of metal baths, slag cover, etc., and also, for studying the heterogeneity of spectrographic standards. The reproducibility of the average content of a material in a metallic bath or slag cover is characterized by a total error:

$$\sigma_{\Sigma} = \sqrt{\frac{\sigma^2_{\text{reproducibility}}}{n} + \sigma^2_{\text{heterogeneity}}}. \qquad (8)$$

Here $\sigma_{\text{reproducibility}}$ is the reproducibility error for a single analysis; n is the number of replicates on which the analysis is based: $\sigma_{\text{heterogeneity}}$ is the root square deviation characterizing the heterogeneity of the test material. Samples were taken from different parts of the material being studied, and each sample analyzed in replicate. Analytical results for each test sample are written in any one column of Table 1, so that the dispersion between columns is determined by the heterogeneity of the material. If $\sigma^2_{\text{heterogeneity}} > \sigma_{\text{reproducibility}}$, then it is clear that there is no need to make several replicate express determinations of a metallic bath and slag crust, since this does not lead to an essential improvement in the error in equation (8). The value of $\sigma_{\text{heterogeneity}}$ allows one to solve the question regarding the use of one or another express method of analysis, which normally possesses a considerable experimental (methodological) error. The criterion which decides whether it should be possible to use an express method of analysis should be the inequality $\sigma^2_{\text{method}} < \sigma^2_{\text{heterogeneity}}$, and not a simple comparison of express methods with methods used previously.

The technique of comparing the degree of heterogeneity of spectrographic standards taken from different parts of a batch with the reproducibility error obtained by replicate analysis of any one sample chosen at random must be regarded as unsuccessful. In such a case, an estimate of the degree of heterogeneity of the standards must be essentially of a qualitative nature, on account of the heterogeneity which is introduced by random choice of sample for determining $\sigma_{\text{reproducibility}}$. Experiment showed that sometimes the reproducibility error was greater than the heterogeneity error [14], although calculation of the errors was carried out on a large population (this only indicates an unfortunate choice of sample for determining the reproducibility). The use of analysis of variance in this case allows one to determine with reliability the heterogeneity error and to evaluate its significance by taking into account the reproducibility error.

During studies of the effect of several factors and their interaction tables of variance are compiled so that the dispersion along the column is determined by one factor while dispersion between columns is determined by another. Dispersion determined by the reproducibility in this case will be determined inside the table squares, in which are included the results of several replicates.* Such analysis will give: the reproducibility error, errors determined by the action of each factor taken separately, and errors determined by the interaction of these factors.

This type of analysis of variance can be used in the following cases: 1) for the study of the degree of standardization of analytical methods during interlaboratory control of several samples carried out simultaneously 2) for the complex study of the action of the time factor on analytical results of samples differing in composition; 3) for studying the effect of the characteristics of the physical composition of test samples (heat treatment, annealing, cold hardening, ageing, etc.) on the results of spectrographic analysis of several test samples differing in composition; 4) for the simultaneous study of the effect of acidity and third elements and their interaction on the results of spectrographic analysis of solutions; 5) for the study of the common action of acidity and temperature at which test samples are dissolved on the results of colorimetric analysis of SiO_2, etc..

Of special interest is the use of a complex scheme of analysis of variance for interlaboratory control when several test samples differing in composition are sent to different laboratories. First of all, in calculating the errors involved in interlaboratory control, it is essential to reject results from those laboratories whose analyses deviate grossly from the means of results obtained by other laboratories, so that the results of these laboratories can be subjected to a special study later. Gross deviations can be evaluated by means of the following equation [15]:

$$|x_{n+1} - \bar{x}| \leqslant t\sigma \sqrt{\frac{n+1}{n}}. \qquad (9)$$

Here, x_{n+1} is the analytical result of the n + 1th; laboratory whose analysis differs considerably.; $\bar{x}$, the mean for all the other n laboratories; σ – root square deviation with respect to this mean; t is given by Student's distribution. Having set a given significance level, it is possible by using equation (9) to determine the limits of acceptable deviations. Further, it is necessary to establish that there is no relation between $\sigma_{\text{reproducibility}}$ and concentration of test component, and to solve the problem of whether intralaboratory reproducibilities in the various laboratories differ essentially from one another. This latter problem can be most easily resolved by using F-distribution, as shown in the example earlier in this article.

If, during interlaboratory control, use is made of a series of standards or standard samples, then, using analysis of variance, it is possible to obtain the following errors: the reproducibility error ($\sigma_{\text{reproducibility}}$), an error connected with the characteristics of the chemical composition of test samples ($\sigma_{\text{random chemical}}$) (in the case of spectrographic analysis – $\sigma_{\text{phys.}}$), an error determined by characteristics of the work in various laboratories (σ_{lab}), an error determined by interaction between the last two factors ($\sigma_{\text{interaction}}$), and a constant experimental error – a. If a sample of unknown composition is subjected to interlaboratory control, then analysis of variance makes it possible to determine only the following values: $\sigma_{\text{reproducibility}}$, σ_{lab}, and $\sigma_{\text{interaction}}$.

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* The technique used for calculation in the case of complex analysis of variance is not given here; it has been treated thoroughly in [4].

Results are given in [10], for the determination of interlaboratory reproducibility by means of the scheme described here in the case of determinations of carbon in a catalyst. For test samples with extreme values of the concentration 1.6-0.23%, the following errors were obtained: $\sigma_{\text{reproducibility}} = 0.026$, $\sigma_{\text{lab.}} = 0.033$, $\sigma_{\text{interaction}} = 0.022$. The total error for interlaboratory control σ_{Σ} proved to be equal to 0.05%; during treatment of results from 11 laboratories, those from 4 laboratories were rejected, since their results were incommensurable with the mean results obtained by the remaining laboratories. If one takes into account the results from all laboratories then $\sigma_{\Sigma} = 0.079\%$.

Results are given in [11], of interlaboratory checks which were all carried out on one sample, in which the acetyl content (39.04%) of cellulose acetate was determined. Calculation gave the following results:

Reproducibility error of a single determination	0.068%
Error introduced by the time factor	0.068%
Error introduced by individuality of the analyst	0.026%
Error introduced by the characteristics of the work of various laboratories	0.251%
Total error of the various laboratories	0.270%

Both these examples demonstrate that in the general balance of errors, the error determined by the characeteristics of the work of a laboratory plays an important part. Meanwhile, GOST (State Standards) as our work shows [16], only takes into account intralaboratory reproducibility error.

In the course of analysis, during a study of the effect of some factor or other, one often has to deal with effects comparable in magnitude with the reproducibility error for a single analysis. Normally, the analyst is compelled to restrict himself to observing the effect of some one, randomly chosen level of the factor being studied. In such a case he may, with a probability of 50%, find a value $\geq 0.67\sigma_{\text{fact.}}$ or a value $\leq 0.67\sigma_{\text{fact.}}$ In the first instance, the effect of the factor being studied will be detected without much trouble; in the second case, in order to establish the actual existence of the factor being studied, it may be necessary to carry out dozens of experiments. Even when this large amount of work has been carried out the result obtained will be of a special character, since they can only be related to a randomly chosen level for the factor being studied. The use of analysis of variance and the setting up of complex experiments allows one, with the minimum possible amount of experimental work, to carry out simultaneously a study of the various levels of the factors in which we are interested, and their interactions, and thus get results which are of a more general character.

Analysis of variance is not the only possible statistical method of studying analytical errors. A few authors have recommended the use of the method of least squares for this purpose [17-21], particularly, when it is a question of introducing corrections. Let us consider two series of values $x_1, x_2, \ldots\ldots x_n$ and $y_1, y_2, \ldots\ldots y_n$; the first set may have been obtained by means of a particularly accurate method or they may be guaranteed results, while the second series may be results obtained on the same samples by approximate methods. By using the method of least squares it is possible to establish a linear relation between these two series of values:

$$y = Bx + A. \tag{10}$$

In this case, experimental error can be split up into a constant, absolute error A, which is independent of the composition of test material, and an error proportional to the concentration of the test component, which is taken into account by the coefficient of proportionality B. Corrections can be applied analytically by using equation (10), the parameters of which are determined by the method of least squares, or graphically. During studies of experimental errors by the method of analysis of variance we used relative errors; accordingly, the value of B in equation (10) will be determined by a constant relative error a, while the value of A enters as a part of the error $\sigma_{\text{random chemical}}$. The fundamental semiempirical equation for quantitative spectrographic analysis ($\log R = b \log c + \log a$) can be considered from a formally mathematical point of view as a special case of this method. Application of corrections, on the basis of equation (10), can of course only be made if one is sure that the values of A and B do not change with time; here we return to a problem which must be solved by analysis of variance.

A number of analytical problems can be solved both by the method of least squares and by analysis of variance. The latter method, generally speaking, is, however, more flexible and of more universal application.

The examples given in this article show that results obtained during a study of analytical errors, and during their interpretation, depend essentially on the method used for calculation; consequently, it is extremely important when dealing with such questions to have a clearly defined standardization of both the methods of calculation and of the terminology. This is particularly important at the moment in connection with the widespread development and introduction into practice of new physical methods of analysis. The simultaneous existence of several methods which differ in principle from each other, and which have been specified by GOST, is possible only as long as one is quite clear on the methods of evaluating experimental analytical errors.

In conclusion, I should like to thank V. G. Pines and S. A. Genshaft for material used in compiling Tables 2 and 3.

SUMMARY

Analysis of variance can be recommended as a basic method of checking on the degree of standardization of analytical methods during interlaboratory control, for the determination of experimental errors, for studying the instability of results of determinations with time, for checking on the degree of heterogeneity of test materials and standards, for studying the effect of separate factors on the results of the determination, etc.

The author recommends the publication of a special State Standard (GOST) entitled "Analytical Errors, Their Classification, Methods of Treating Experimental Data, Establishment of Confidence Limits, etc.,"* in order to standardize methods of evaluating analytical errors.

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* At the same time it is suggested that the question of including a course of the mathematical theory of errors in the syllabus of high schools, and higher education establishments training analysts, should be put before the Ministry of Higher Education.

** [Original Russian pagination. See C. B. Translation.]

*** [As given in original. Spelling inconsistent with spelling in text – Editor's note.]

INVESTIGATION OF THE COMPLEX COMPOUNDS OF THORIUM AND AMINOPOLYCARBOXYLIC ACIDS BY MEANS OF HIGH FREQUENCY TITRATION

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There are only two published references to the interaction of thorium with complexones; with nitrilotriacetic and ethylenediaminetetracetic acids respectively. Brintzinger [1] isolated compounds in which the ratio of thorium to ethylenediaminetetracetic acid was equal to one. The author assumes that in this compound thorium is bound as a salt $[CH_2-N(CH_2COO)_2]_2Th(2H_2O$ or $1/2\ H_2O)$.

Nevertheless, later, on the basis of potentiometric titration of a mixture of thorium and Complexone III with alkali, Cabell [2] came to the conclusion that three complexes exist in solution: $Th\gamma$, $Th\gamma_2$ and $Th_2\gamma$, where γ is the ethylenediaminetetracetic acid residue; in his opinion the most stable of these compounds, in acid media, is the complex $Th\gamma$. Cabell's results were later confirmed by Hara and West [3], who used high frequency titration. Schwarzenbach, Gut, and Anderegg [4], determined the formation constant of the complex $Th\gamma$ polarographically and showed it to be 3.0×10^{23} ($pK = 23.2 \pm 0.1$).

The high stability of the complex formed between thorium and Complexone III allows one to determine thorium accurately by the complexometric method, even in relatively acid media. Thus, Fritz and Ford [5] (also Ter Haar and Bazen [6]) used Complexone III for titrimetric determination of thorium in the presence of Alizarin Red S. Pyrocatecholsulfonphthalein has also been used as indicator [7]. Haar and Bazen showed that the reaction between thorium and complexone goes quantitatively at pH 2.8-4.3. Malmstadt and Gohrbandt [8] determined thorium by spectrophotometric titration with Complexone III in the presence of cupric nitrate as indicator. Prshibil [9] used Complexone III as a masking agent for separating thorium from uranium, the latter being precipitated with ammonia.

Data relevant to the behavior of thorium with sodium nitrilotriacetate is scant. We are only aware of one paper [2] in which results are given for the potentiometric study of complexes of thorium and Trilon A. The author points out that the most stable complex is formed for a ratio of metal to complexone of 1:2.

We thought it would be of interest to investigate, by the method of high frequency titration, the complex compounds formed between thorium and a number of new complexones, particularly in view of the fact that the spatial distribution of the complex-forming groups in some of them leads one to assume the existence of more stable complex thorium compounds than is possible with the widely used ethylenediaminetetracetic acid.

Below we have given the results of experiment [10] which were obtained independently from Hara and West during a study of the interaction of thorium with complexones. All measurements were carried out on a high frequency setup (36 megacycles) constructed in the Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR, by V. A. Zarinsky and D. I. Koshkin [11-13]. Test solutions were placed in a cell which was in the form of a thin-walled glass beaker. Changes in the chemical composition of the solution which occurred during titration affected the active conductivity of the solution, and determined the value of the total cell conductivity. Relative current changes were measured with a micro-ammeter. Titrations were all carried out at emperature. The equivalence point was determined graphically. Current in microamperes was plotted he ordinate, and volume of reagent used for titration,(or alternatively,the molecular ratio of reactants) the abscissa..

y analogy with potentiometric investigations, the study of the behavior of thorium compounds with com- es was carried out by: 1) titration of a mixture of thorium salt and complexone with alkali, and 2) titra- a thorium salt with a solution of the appropriate complexone.

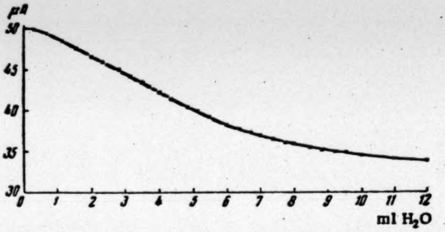
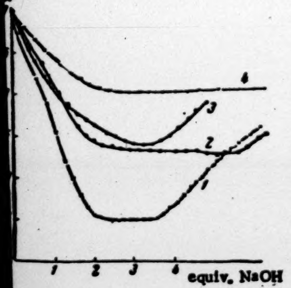


Fig. 1. Relation between conductivity and volume of solution in the cell.

both cases there was observed a change in conductivity of the system with changes in the hydrogen ion ation of the solution, in the first instance as a result of titration of hydrogen ions by alkali, and in the nstance, as a result of hydrogen ions gradually released during interaction between the thorium salt and one.

eliminary tests showed that conductivity changes in the solution could be attributed, not only to the ction, but were, to a considerable extent, the result of changes in the volume of solution in the titra- . In order to evaluate this latter effect, a curve (Fig. 1) was drawn relating conductivity of the system lume of solution in the cell. 50 ml of distilled water was first introduced into the cell, and the value rrent measured on each subsequent addition of more water. Taking ethylenediaminetetracetic acid as ple, we have given in Figs. 2 and 3 curves in which this volume effect has been either taken into or left out. It is evident from these figures that the volume of the system influences the conductivity bly; consequently, in all subsequent tests, the original volume used for titration was 50 ml; the volume s taken into account in constructing all curves.



tration of a mixture of thorium chloride y with alkali (no corrections for volume lied) Ratios of thorium: Complexone 1) 2; 3) 2 : 1; 4) 1 : 3.

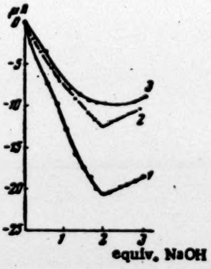


Fig. 3. Titration of a mixture of thorium chloride and Na_2H_2y with alkali (corrections applied for volume effect). Ratios of thorium: Complexone 1) 1 : 1; 2) 1 : 2; 3) 2 : 1.

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0.084 M alkali solution, free of carbon dioxide, was used for titration.

The curves obtained are analogous to conductometric titration curves, as observed earlier [12].

Tests with Salts of Nitrilotriacetic Acid* and Uramyldiacetic** Acid (Na_2HX; Na_2HUr)

10 ml of a 1×10^{-2} M solution of thorium chloride was placed in a cell, followed by additions of 1×10^{-2} M solutions of the addendum until their molar ratio with the thorium salt was 1 : 1; 1 : 2; 1 : 3, respectively. The solutions thus obtained were titrated with alkali. In the case of tribasic aminopolycarboxylic acids, in contrast to quadribasic ones, the maximum change in conductivity was observed during titration of a mixture of thorium chloride with tribasic acid at a ratio of metal to complexone of 1 : 2 (Fig. 4). In the case of uramyldiacetic acid curves similar to those given in Fig. 4 were obtained.

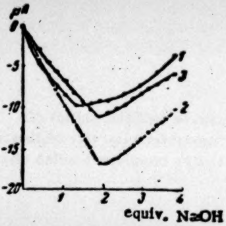

Fig. 4. Titration of a mixture of thorium chloride and Na_2HX with alkali. Ratios of thorium: Complexone 1) 1 : 1; 2) 1 : 2; 3) 1 : 3.

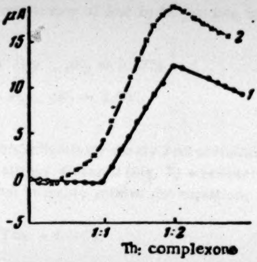

Fig. 5. Titration of thorium chloride with sodium nitrilotriacetate (1), and sodium uramyldiacetate (2).

On the titration curve obtained for 2×10^{-3} M thorium chloride with a 5×10^{-2} M solution of disubstituted sodium nitrilotriacetate or sodium uramyldiacetate (Fig. 5), the conductivity maximum also corresponds to a molar ratio of thorium to complexone of 1 : 2. It should however be noted that at ratios of thorium to complexone less than or equal to 1 : 1, the conductivity, in cases where the salts of tribasic aminopolycarboxylic acids were used for titration, remained practically constant. This leads one to think that in the given instance, in addition to a complex formed at a ratio of 1 : 2, there is also formed a complex at a ratio of 1 : 1. Presumably the most stable complex is the one formed at a ratio of 1 : 2.

On the titration curves of 4×10^{-3} M solutions of disodium nitrilotriacetate or sodium uramyldiacetic acid respectively, with 5×10^{-2} M thorium chloride (Fig. 6), there is only one well defined break at a ratio of thorium to addendum of 1 : 2. The interactions are described by the following equations:

$$Th^{4+} + 2\,HX^{2-} \rightarrow ThX_2^{2-} + 2H^+;$$

$$Th^{4+} + 2HUr^{2-} \rightarrow ThUr_2^{2-} + 2H^+.$$

Experiments with Salts of Ethylenediaminetetracetic Acid (Na_2H_2Y, Na_4Y)

During titration of a mixture of thorium chloride and disodium ethylenediaminetetracetate with alkali, 10 ml of 1×10^{-2} M thorium chloride was added to the titration cell; this was followed by various amounts of 1×10^{-2} M complexone solution, corresponding to ratios of thorium to addendum of 2 : 1, 1 : 1, and 1 : 2. During interaction of the thorium salt with the disubstituted salt, hydrogen ions were released which were titrated with the sodium hydroxide. On addition of NaOH, as a result of a decrease in hydrogen ion concentration, the conductivity of the system dropped, and at the equivalence point reached its minimum value. It is clear from Figs. 2-3 that the sharpest break is obtained during titration of a mixture of thorium chloride and complexone in the ratio 1:1. In this case, as a result of the absence of excess of either of the components, a maximum change in the conductivity of the system was observed. Since, under these conditions, exactly two equivalents of alkali were used for titration, this leads one to conclude correctly that a stable complex of thorium is formed which has a ratio of thorium to Complexone of 1:1. The interaction is described by the relation: $Me^{4+} + H_2\gamma^{2-} \rightarrow Me\gamma + 2H^+$. Nothing definite can be said about the presence of compounds with other ratios of components.

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* Prepared in the Institute of Chemical Reagents (R. P. Lastovsky laboratory).

** Prepared in the All-Union Scientific Research Chemico-Pharmaceutical Institute (M. N. Shchukina's laboratory).

Direct titration of thorium chloride solution with disodium ethylenediaminetetracetate was carried out as follows. 2×10^{-3}M thorium chloride solution was introduced into the titration cell and titrated with 5×10^{-2}M Complexone. Curve 1 (Fig. 7) shows that thorium reacts with the complexone to form a stable complex at a ratio of thorium to complexone of 1:1. Consequently, in this case also, the process is described by the equation already given. As a result of the release of hydrogen ions during the reaction, the conductivity of the solution increases; it reaches its maximum value at the equivalence point. Addition of excess complexone leads to a decrease in conductivity, presumably as the result of complexing of free hydrogen ions by the complexone:

$$H_2\gamma^{2-} + H^+ \rightleftharpoons H_3\gamma^-.\ pK_2 = 2.672;$$

$$H_3\gamma^- + H^+ \rightleftharpoons H_4\gamma.\ pK_1 = 1.996.$$

On further addition of complexone to thorium, the conductivity slowly and uniformly decreases. When the tetrasodium salt was used instead of the disodium salt as titrant Curve 2 (Fig. 7) was obtained, which had a clearly defined minimum at a ratio of 1:1. The reaction probably follows the equation:

$$ThCl_4 + Na_4\gamma \rightarrow Th\gamma + 4NaCl.$$

Nevertheless, since the process occurs in alkali media, the possibility of interaction between thorium and complexone to form hydroxy compounds is not excluded.

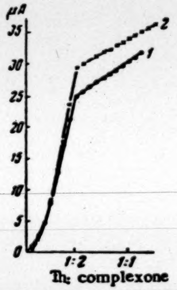

Fig. 6. Titration of sodium nitrilotriacete (1) and sodium uramyldiacetate (2) with thorium chloride.

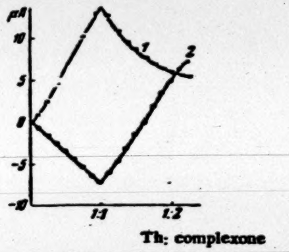

Fig. 7. Titration of thorium chloride with sodium ethylenediaminetetracetate: 1) $Na_2H_2\gamma$; 2) $Na_4\gamma$; 3) • titration of $Na_2H_2\gamma$ with thorium chloride.

Such a clearly defined break in conductivity at the equivalence point was not observed on the titration curve for a 2×10^{-3}M complexone solution with 5×10^{-2}M thorium chloride, but a break was clearly observable at a ratio of thorium to Complexone of 1:1, which confirmes the equation given above. Before the equivalence point was reached there was a sharp increase in conductivity as a result of liberation of hydrogen ions during the reaction. When the reaction was complete, addition of excess metal had a lesser effect on the conductivity changes of the solution; this led to a break in the curve. The curve obtained thus was similar to that given in Fig. 11 for a number of other aminopolycarboxylic acids.

** (As in original – Publisher's note).

Experiments with Cyclobutane-,* Cyclopentane-,** and Cyclohexane-Diaminetetracetic Acids (H_4B, H_4P, H_4Hex)***

Titration conditions were the same as for sodium ethylenediaminetetracetate. During titration with alkali of solutions containing a mixture of thorium chloride with any of the complexones indicated (the disubstituted sodium salts) in ratios of 1:1, 1:2, and 2:1, it was observed (Fig. 8) **** that the maximum change in conductivity of the solution occurs at a molar ratio of thorium to Complexone of 1:1 for each of the Complexones. The reactions are apparently described by the equations:

$$Th^{4+} + H_2Hex^{2-} \rightarrow ThHex + 2\,H^+;$$
$$Th^{4+} + H_2P^{2-} \rightarrow ThP + 2H^+;$$
$$Th^{4+} + H_2B^{2-} \rightarrow ThB + 2H^+;$$

In the case of titration of thorium chloride with disodium or tetrasodium cyclohexane- or cyclopentanediaminetetracetate, clear cut changes in conductivity are observed on the titration curves (Figs. 9-10) at the equivalence point which correspond to a molar ratio of thorium to either of the Complexones of 1:1. On addition of further Complexone, only a smooth decrease in conductivity was observed.

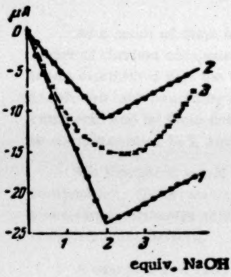

Fig. 8. Titration of a mixture of thorium chloride and Na_2H_2P with alkali. Ratio of thorium: Complexone 1) 1:1, 2) 1:2; 3) 2:1.

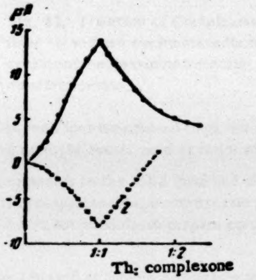

Fig. 9. Titration of thorium chloride with sodium cyclopentanediaminetetracetate: 1) Na_2H_2P; 2) Na_4P.

Titration curves for thorium with each of the salts studied were different in shape (Fig. 11). A break is observed at a ratio of 1:1 instead of a maximum.

Curves obtained with cyclohexane-, with cyclopentane-, and cyclobutanediaminetetracetates were similar to those obtained with ethylenediaminetetracetate. This indicates that thorium forms stable complexes with salts of the aminopolycarboxylic acids mentioned for ratios of thorium to complexone of 1:1. Results obtained by high frequency titration are in agreement with those of potentiometric experiments carried out by Cabell on sodium ethylenediaminetetracetate and sodium nitrilotriacetate, and also with the results for sodium uramyldiacetate, cyclohexane-, cyclopentane-, and cyclobutanediaminetetracetates which we obtained.

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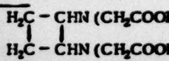
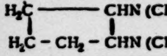
* 

** 

*** All these complexones were prepared in the All-Union Scientific Research Chemico-Pharmaceutical Institute (M. N. Shukina's laboratory).

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Similar curves were also obtained with cyclobutane- and cyclohexanediaminetetracetates.

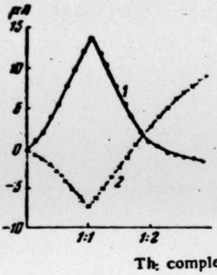

Fig. 10. Titration of thorium chloride with sodium cyclohexanediaminetetracetate: 1) Na_2H_2Hex; 2) Na_4Hex.

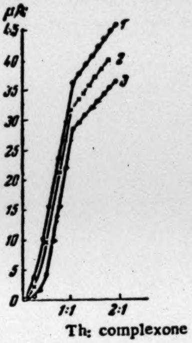

Fig. 11. Titration of Complexone with thorium chloride: 1) sodium cyclobutanediaminetetracetate; 2) cyclopentanediaminetetracetate; 3) cyclohexanediaminetetracetate.

As a result of these investigations of the behavior of thorium compounds with complexones, it was established that the most stable complexes in solution are formed by ethylenediaminetetracetic acid and by those complexones which contain six, five, and four membered rings, for a ratio of thorium to complexone of 1: 1, and also by nitrilotriacetic acid and uramyldiacetic acid at ratios of 1: 2.

We thought it would be of interest to isolate these compounds in the solid form and characterize their composition. Unfortunately, we only had small amounts of cyclopentanediaminetetracetic acid and cyclobutanediaminetetracetic acid at our disposal; consequently, it was not possible to prepare compounds of these materials with thorium.

A compound of thorium with nitrilotriacetic acid was isolated at a ratio of thorium to complexone of 1: 2. The pH of the mixture was adjusted to 8.2 with ammonia before addition of methanol and ether. The compound isolated was analyzed for its contents of thorium, nitrogen, and water (Table 1).

TABLE 1

Analysis of the Compound formed between Thorium and Nitrilotriacetic Acid

Component determined	Found in %	Calculated as:	
		$(NH_4)_2[ThX_2]\cdot 4H_2O$	$(NH_4)_2[ThX_2]\cdot 5H_2O$
Thorium (as metal)	32.1	32.4	31.6
Total nitrogen	8.1	7.8	7.6
Amine nitrogen	3.9	3.9	3.8
Water	10.7	10.0	12.3

The electrical conductivity of a 10^{-3} M solution of the complex was 306 mhos, which is closest to the value of the specific electrical conductivity (250 mhos) corresponding to the presence of three ions in solution. On passing a solution of the compound isolated through a cation exchange resin and an anion exchange resin, it was found that the complex ion containing thorium passed completely through the cation exchange resin and was sorbed on the anion exchange resin; consequently this ion has a negative charge. No hydroxyl ions enter into the composition of the complex. Accordingly, the composition of the compound

obtained corresponds most closely to the formula $(NH_4)_2 . [ThX_2] \cdot 4H_2O$.

The compound formed between thorium and uramyldiacetic acid was isolated at a ratio of thorium to complexone of 1 : 2; the pH of the original solution was 8.2. In all, about 300 mg of a material was isolated which was analyzed for its contents of thorium, nitrogen, and water (Table 2).

TABLE 2

Analysis of the Compound formed between Thorium and Uramyldiacetic Acid

Component determined	Found in %	Calculated according to formula	
		$(NH_4)_2[ThUr_2] \cdot 4H_2O$	$(NH_4)_2[ThUr_2] \cdot 5H_2O$
Thorium	27.5	27.2	26.7
Amine nitrogen	2.9	3.3	3.2
Water	9.1	8.9	10.3

The electroconductivity of a 10^{-3} M solution of the compound isolated had a value of 206 mhos, which approximates most closely the value of the specific conductivity (250 mhos) corresponding to the presence of three ions in solution. On passing a solution of the compound through ion-exchange resins, it was established that the complex ion has a negative charge. No hydroxyl ions were detected in the complex. Thus, the composition of the compound isolated corresponds most closely to the formula $(NH_4)_2 . [ThUr_2] \cdot 4H_2O$.

The compound formed between thorium and cyclohexanediaminetetracetic acid was isolated at a ratio of thorium to complexone of 1 : 1.

The pH of the original solution was 9.0. The analytical results for this compound are given in Table 3. The electrical conductivity of a 10^{-3} M solution of the complex was 150 mhos, which indicates the presence of two ions in solution. On passing a solution of this complex through ion exchange columns, it was established that the complex ion carries a negative charge. Titration of a solution of the compound isolated with acid showed the presence of one hydroxyl group. Thus, the composition of the compound isolated corresponds most closely to the formula $NH_4[Th\,Hex\,OH] \cdot 5H_2O$.

TABLE 3

Analysis of the Compound formed between Thorium and Cyclohexanediaminetetracetic Acid

Component determined	Found in %	Calculated according to formula	
		$NH_4[ThHexOH] \cdot 5H_2O$	$NH_4[ThHex(OH)_2]^{2-} \cdot 5H_2O$
Thorium	33.3	33.1	31.6
Amine nitrogen	2.1	2.0	3.9
Carbon	24.7	24.0	22.9
Hydrogen	5.0	5.3	5.2
Water	12.8	12.9	12.2

The compound of thorium with ethylenediaminetetracetic acid was isolated at a ratio of thorium to complexone of 1 : 1. The initial pH value of the solution of the mixture of thorium and complexone was 7.0. Compounds of thorium with the sodium and ammonium salts of the complexone were isolated.

Analytical results are given in Tables 4 and 5.

The electrical conductivity of a 10^{-3} M solution of the complex isolated from the ammonium salt was 143 mhos (pH 6.5), while that obtained on using the sodium salt of the complexone was 108 mhos. By using

TABLE 4

Analysis of the Compound formed between Thorium and Ammonium Ethylenediaminetetracetate

Component determined	Found in %	Calculated according to formula	
		$NH_4[Th\gamma OH]\cdot 4H_2O$	$(NH_4)_2[Th\gamma(OH)_2]\cdot 4H_2O$
Thorium	36.9	37.0	35.0
Total nitrogen	6.5	6.7	8.4
Amine nitrogen	2.2	2.16	4.2
Carbon	19.8	19.13	18.1
Hydrogen	4.1	3.99	4.5
Water	11.0	11.5	10.9

TABLE 5

Analysis of the Compound formed between Thorium and Sodium Ethylenediaminetetracetate

Component determined	Found in %	Calculated according to formula	
		$Na[Th\gamma OH]\cdot 4H_2O$	$Na_2[Th\gamma(OH)_2]\cdot 4H_2O$
Thorium	35.5	36.7	34.5
Total nitrogen	4.0	4.4	4.2
Amine nitrogen	0.1	–	–
Carbon	19.2	19.0	17.8
Hydrogen	3.7	3.3	3.1
Water	12.6	11.8	10.7

ion-exchange resins, it was established that thorium is located in the anion. Titration of solutions of these compounds with hydrochloric acid indicated the presence of one hydroxyl group in the molecule of the complex.

Consequently, the composition of the compounds isolated can be represented most closely by the formulas:

$$NH_4[Th\gamma OH]\cdot 4H_2O \text{ and}$$

$$Na[Th\gamma OH]\cdot 4H_2O.$$

Results of physicochemical studies on the composition of the complex compounds formed with aminopolycarboxylic acids were confirmed by the results of preparative methods.

In order to make use of these stable complex compounds in analysis, it is next necessary to make a study of the selectivity of their reactions. Despite the fact that complexones are not very selective, nevertheless the compounds they form differ in stability and, by suitable choice of pH, it is possible, in many instances, to avoid interference from other ions.

The practically identical behavior of thorium during its interaction with cyclohexane- and cyclopentanediaminetetracetic acids leads one to conclude that it should be possible to use these complexones together with ethylenediaminetetracetic acid during complexonometric determination of thorium, and also for masking thorium when it is necessary to determine certain impurities in thorium. The advantage of aminopolycarboxylic acids over other complexing agents is that the formation of the corresponding complexonate proceeds immediately, while the components react in strictly stoichiometric proportions.

SUMMARY

1. The interaction of thorium with a number of aminopolycarboxylic acids has been studied.

2. It has been established by the method of high frequency titration, and confirmed by the results of preparative methods, that thorium forms complex compounds with uramyldiacetic acid and nitrilotriacetic acids at a molar ratio of thorium to the complexones of 1 : 2 (at pH 8.2 thorium reacts with nitrilotriacetic acid to give $(NH_4)_2[ThX_2]\cdot 4H_2O$ while with uramyldiacetic acid it gives $(NH_4)_2[ThUr_2]\cdot 4H_2O$).

In the case of reactions between thorium and cyclohexane-, cyclopentane-, cyclobutane-, and ethylenediaminetetracetic acids, complexes are formed at a molar ratio of thorium to complexone of 1 : 1 (at pH 7.0 thorium gives with ethylenediaminetetracetic acid a compound with the formula $NH_4[ThYOH]\cdot 4H_2O$, while at pH 9.0 it gives with cyclohexanediaminetetracetic acid a compound which can be represented by the formula $NH_4[ThHexOH]\cdot 5H_2O$).

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EXTRACTION OF URANYL α-NITROSO-β-NAPHTHOLATE AND SEPARATION OF URANIUM FROM VANADIUM AND IRON

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Apart from the well known extractive separation of uranium from nitrate solutions by ether or other solvents, wide use is made of the extraction of sexivalent uranium in the form of its inner-complex compounds with acetylacetone [1-3], dibenzoylmethane [4-7], 8-hydroxyquinoline [8-10], diethyldithiocarbamate [11-12], and other organic reagents. Quadrivalent uranium is readily extracted in the form of its compound with thiophenecarbonyltrifluoroacetone, and as the cupferronate. In the work described here we studied the extraction of uranyl α-nitroso-β-naphtholate, and demonstrated the possibility of separating uranium from vanadium and iron which are complexed as a non-extractable complex with Complexone III.

Tanii, Hosimiya, and Ykeda [13] studied the precipitation of several cations by means of α-nitroso-β-naphthol and found that, in particular, sexivalent uranium is quantitatively precipitated at pH 4.05 - 9.38. American investigators have indicated that uranium gives a precipitate with α-nitroso-β-naphthol which is brownish-red in color and is soluble in amyl alcohol. Extractive separation of uranium as the α-nitroso-β-naphtholate was not studied.

Optimum Conditions for Extracting Uranyl α-Nitroso-β-Naphtholate

The concentration of the stock solution of uranyl nitrate was 1 mg U/ml. The reagent used was a 2% alcoholic solution of α-nitroso-β-naphthol.

The procedure used was as follows. A known volume of the uranyl nitrate solution (usually 2 ml) was measured out of a buret into a 50 ml separating funnel, distilled water was added to bring the volume up to a definite value, and then dilute hydrochloric acid or ammonia was added to adjust the pH value. The alcoholic solution of reagent was added separately to the extraction solvent, and the combined solution thus obtained transferred to a separating funnel. After shaking, the organic layer was removed and collected in a small porcelain crucible which had been weighed on a micro-balance. The solvent was carefully removed by evaporation on an air bath; the residue was dried and finally ashed at 900°. The crucible plus residue was allowed to come to constant weight; from the amount of uranoso-uranic oxide obtained the percentage extraction was then calculated.

It was established that at pH 5-6, uranyl α-nitroso-β-naphtholate can be extracted by organic solvents which are immiscible with water; in particular, it can be extracted by isoamyl alcohol.

It is known that the amount of reagent is one of the decisive factors which determine percentage extraction. We evaluated this amount by means of the ratio mols. reagent / mols U_3O_8, since the composition of the compound of UO_2^{2+} with α-nitroso-β-naphthol is not known accurately enough. The results obtained (Fig. 1) show that it is essential to use an excess of reagent, corresponding to a ratio of mols. reagent/mols U_3O_8 of more than 100. In subsequent experiments the amount of α-nitroso-β-naphthol used corresponded to a ratio of 125. When such an excess was used the uranium transferred completely into the isoamyl alcohol at a pH of 5-6, after only one extraction.

Quantitative extraction of uranium by only one extraction (Fig. 2) was achieved at a ratio of volume of organic phase to volume of aqueous phase $v_{org.} / v_{water}$ of 0.20. In subsequent experiments the ratio used was $v_{org} / v_{water} = 0.25$.

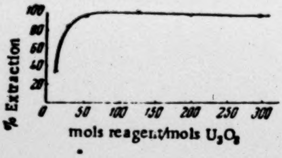

Fig. 1. Relation between percentage extraction of uranyl α-nitroso-β-naphtholate and amount of reagent used.

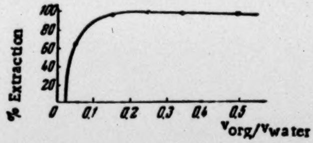

Fig. 2. Relation between percentage extraction of uranyl α-nitroso-β-naphtholate and ratio of volumes of organic phase to aqueous phase.

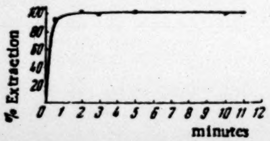

Fig. 3. Relation between percentage extraction of uranyl α-nitroso-β-naphtholate and duration of shaking.

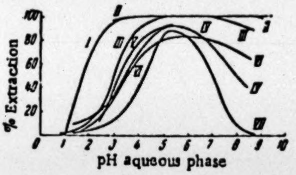

Fig. 4. Relation between percentage extraction of uranyl α-nitroso-β-naphtholate and pH of the aqueous phase and nature of extraction solvent: I) ethyl acetate; II) n-butanol; III) isoamyl alcohol; IV) diethyl ether; V) amyl acetate; VI) benzene; VII) chloroform.

Distribution equilibrium is attained very rapidly. Two minute shaking ensures complete quantitative separation of uranium (Fig. 3).

A study of the relation between percentage extraction and pH of the aqueous phase was carried out in the presence of benzene, xylene (mixture of the isomers), chloroform, carbon tetrachloride, dichloroethane, diethyl ether, ethylacetate, amyl acetate, isoamyl alcohol, n-butanol, and cylcohexanone. In the case of benzene, carbon tetrachloride, and cyclohexanone, formation of layers was accompanied by formation of a film which was difficult to break down; in the case of xylene, a precipitate formed.

Curves relating percentage extraction to pH of the aqueous layer in the presence of the seven best extraction solvents are given in Fig. 4. The best extraction solvents for uranyl α-nitroso-β-naphtholate proved to be n-butanol and ethyl acetate, which quantitatively extracted uranium in the pH range 3.0-8.5, and isoamyl alcohol which extracted uranium at a pH of 4.5-7.5 (Fig. 4). Despite the narrower pH range for extraction, isoamyl alcohol is more convenient since it is readily available and is less soluble in the water; this solvent was accordingly used for all subsequent work.

Changes in temperature from 0 to 100° had no effect on extraction of uranyl α-nitroso-β-naphtholate (Table 1). In the remaining experiments, room temperature was used.

The presence of chloride and nitrate ions at concentrations ranging from 0 to 0.2 mol/liter do not deleteriously affect extraction of uranium.

Separation of Uranium From Iron and Vanadium

The procedure used for removing uranium from vanadium and iron was left basically unchanged; the vanadium and iron contents of the organic phase were determined gravimetrically: vanadium as V_2O_5, and iron as Fe_2O_3. During simultaneous extraction of vanadium or iron and uranium, the contents of vanadium and iron in the organic phase were determined by difference. The stock solutions used were NH_4VO_3 (1 and 15 mg/ml V) and $Fe_2(SO_4)_3$ (1 mg/ml Fe). In addition, solutions of vanadium sulfate with concentrations of 1 and 15 mg/ml were used. There are published references [14, 15] which indicate that such a solution at pH < 4 is very stable to oxidation even on keeping for a long time.

TABLE 1

Relation Between Percentage Extraction of Uranyl α-Nitroso-β-Naphtholate and Temperature

Temperature, °C	U_3O_8 taken in mg	U_3O_8 found in mg	Percentage extraction
0–5	2.32	2.31	100
20	2.32	2.33	100
60	2.32	2.27	98
100	2.32	2.34	101

Separation from Vanadium. Extraction of vanadium with isoamyl alcohol under the conditions which had been established to give optimum extraction of uranium was investigated in relation to the pH of the aqueous phase. It was found that quinquevalent vanadium was extracted to the extent of 10-12%, while quadrivalent vanadium was extracted to the extent of 43-48%.

Separation, however, can readily be achieved if vanadium in the quadrivalent state is complexed by addition of Complexone III. With the latter, sexivalent uranium only gives a very unstable compound which is probably either the normal salt [16], or an unstable complex [17]. Quinquevalent vanadium does not give a stable complex with Complexone III; nevertheless, it can be readily reduced with sulfur dioxide to the quadrivalent state, which is firmly complexed by the complexone. According to Schwarzenbach and Sandera [18], -logarithm K = 18.4. Further, vanadium at low concentrations can be reduced to the quadrivalent state at pH 1-2 by Complexone III itself, as Malinek [19], and also Paley [20], have shown.

Extraction in the presence of Complexone III, at various values of the pH of solutions of uranium, quinquevalent and quadrivalent vanadium, was studied separately. 25 mg of complexone was taken for each mg of element. The results obtained are represented in Fig. 5.

The pH range at which complete removal of uranium in the presence of Complexone III (Curve 1) is achieved is displaced to more alkaline values (from 4.5-7.5, to 6.5-9.5). This can be explained by the formation of an unstable complex of the uranyl ion with Complexone III; the maximum stability of this complex, according to Hara and West's results [17], is exhibited precisely within the pH range at which uranyl α-nitroso-β-naphtholate is extracted (pH 5-6).

As can be seen from Fig. 5, at pH 6.5-9 all the quadrivalent vanadium remains in the aqueous phase, while uranium is completely extracted. This indicates that it is possible to separate these metals by extracting uranyl α-nitroso-β-naphtholate at a pH of 6.5-9 under the conditions indicated above.

At least a four-fold excess of Complexone III is required for complexing the quadrivalent vanadium. The presence of an appreciable amount of complexone does not affect uranium extraction deleteriously.

The results obtained are given in Table 2. It is obvious that it is possible to separate uranium from three times its amount of vanadium. When greater amounts of vanadium are present, some of the vanadium is extracted.

Separation from Iron. In the absence of Complexone III, under conditions which ensure complete extraction of uranyl α-nitroso-β-naphtholate, trivalent iron is completely extracted. Nevertheless, addition of Complexone III to complex the trivalent iron makes possible a separation of iron from uranium.

Trivalent iron forms a very stable complex with sodium ethylenediaminetetracetate (-logarithm k = 25.1). In Fig. 6 is given a curve depicting extraction of iron in the presence of sodium ethylenediaminetetracetate with α-nitroso-β-naphthol and isoamyl alcohol; a similar curve for uranium is shown for comparison.

In the pH range 6.5-8, uranium is extracted quantitatively, while iron remains in the aqueous phase. A 4-5-fold excess of complexone III is sufficient for complexing the iron.

Uranium was removed from solutions containing iron at a pH of 7.0-7.5. To ensure reliable separation, the organic layer, after extraction with isoamyl alcohol, was removed and washed with a dilute aqueous solution of Complexone III. Uranium was separated from ten times its amount of iron.

TABLE 2

Separation of Uranium from Vanadium

Ratio U : V	Taken in mg			U_3O_8 found in mg	Percentage extraction	Error	
	U_3O_8	VO_3	complexone III			In mg	In %
1 : 1	2.32	3.04	50	2.34	101	+0.02	+ 1
1 : 1	2.32	3.04	50	2.27	98	−0.05	− 2
1 : 1	2.32	3.04	50	2.27	98	−0.05	− 2
1 : 1	2.32	3.04	50	2.33	100	+0.01	0
1 : 3	2.32	9.12	150	2.27	98	−0.05	− 2
1 : 10	2.32	31.12	500	2.99	129	+0.67	+29
1 : 10	2.32	31.12	500	2.94	127	+0.62	+27
1 : 10	2.32	31.12	500	2.96	128	+0.64	+28

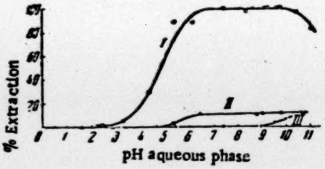

Fig. 5. Relation between percentage extraction of compounds of U(VI), V(V), and V(IV) with α-nitroso-β-naphthol in the presence of Complexone III for various pH values of the aqueous phase: I) extraction of U; II) extraction of V(V); III) extraction of V(IV).

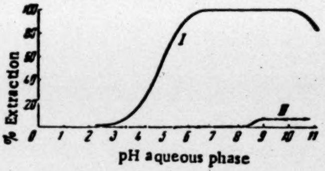

Fig. 6. Relation between percentage extraction of Fe(III) α-nitroso-β-naphtholate in the presence of Complexone III, and pH of the aqueous phase. Curve for extraction of U is included for comparison. I) extraction of U; II) extraction of Fe.

We obtained qualitative indications that it is possible to separate uranium from thorium by masking the latter with Complexone III and extracting uranium as uranyl α-nitroso-β-naphtholate. There are published indications [21] that the complex formed between thorium and Complexone III is very stable (-logarithm k = 23.2). When no complexone is present, a considerable amount (about 28%) of thorium is extracted in the presence of α-nitroso-β-naphthol. It is also possible to separate uranium from aluminum and zinc, which do not react with α-nitroso-β-naphthol.

SUMMARY

1. Sexivalent uranium can be quantitatively extracted as uranyl α-nitroso-β-naphthol from aqueous solutions by means of organic solvents which are immiscible with water.

2. Optimum conditions for extracting uranyl α-nitroso-β-naphthol have been established. The best extraction solvents (of those studied) are isoamyl alcohol, n-butanol, and ethyl acetate; n-butanol and ethyl acetate extract uranium completely over a pH range of 3.0 to 8.5, while isoamyl alcohol is best over the range 4.5 to 7.5.

3. It has been demonstrated that it is possible to separate uranium from vanadium and iron by extracting uranium as uranyl α-nitroso-β-naphtholate with isoamyl alcohol from neutral solutions, after addition of Complexone III.

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THE USE OF A ZINC PHOSPHATE ELECTRODE IN POTENTIOMETRIC ANALYSIS

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At the moment there is no accurate and rapid method of determining calcium and magnesium when they are simultaneously present. There are several published methods for determining calcium in the presence of magnesium by potentiometric titration [1-3]; magnesium is not determined by these methods.

We have succeeded in carrying out potentiometric titration of calcium and magnesium with potassium phosphate using a zinc-phosphate electrode for PO_4^{3-} ions:

$$Zn_3(PO_4)_2 + 6e \rightleftharpoons 3Zn_{solid} + 2PO_4^{3-}.$$

The zinc phosphate electrode was prepared by electrolytic parkerizing (phosphatization) of metallic zinc with a current of a few milliamps (20-30) in the course of 3-4 hours, in a dilute solution of sodium phosphate; the electrode was finally left to stand in the same solution for 24 hours. When solutions containing calcium and magnesium ions are titrated by means of an electrode of this type, there is an appreciable jump at the equivalence point.

The potential of the phosphatized electrode in test solutions was measured during titration by means of a compensation method, using a PPTVI potentiometer of the second type. The reference electrode was a calomel electrode.

We proceeded on the assumption that if we could succeed in titrating calcium and magnesium salts completely by means of phosphate solutions, then, since the solubility products of calcium phosphate and magnesium phosphate differ appreciably from each other, it should be possible to find conditions whereby magnesium and calcium could be determined separately.

Various amounts of calcium and magnesium ions were titrated with potassium phosphate solutions; the solution was agitated continuously by means of a stirrer. The curve relating potential to volume of added precipitant during potentiometric titration of magnesium ions is given in Fig. 1, while that for calcium is shown in Fig. 2.

The equivalence point was established by constructing curves within the coordinates $\Delta E/\Delta V - V$, where V is the volume of potassium phosphate solution added, while ΔV is the change after the last addition. The equivalence point was established on the basis of the position of the maximum on the curve (Figs. 1 and 2). Good experimental results were obtained for large concentrations of magnesium and calcium ions; for low concentrations the error was 17% (Table 1).

In order to eliminate titration errors during determination of small amounts of calcium and magnesium ions, we used the method of double addition [4].

1. Two aliquots of a test magnesium solution are taken; the unknown magnesium concentration is designated by x. A known amount C_1 of magnesium (first addition) is added to one of these aliquots; the volume is then made up to 25 ml and the whole titrated with potassium phosphate with continuous stirring of the solution.

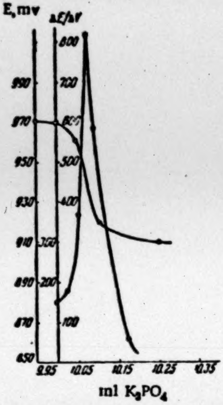

Fig. 1. Potentiometric titration of magnesium ions with the zinc-phosphate electrode. The equivalence point lies at 10.08 ml of 0.2095 N K_3PO_4. 25.70 mg of Mg^{2+} was titrated with an error of 0.39%.

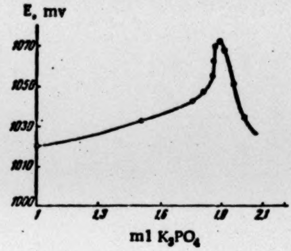

Fig. 2. Potentiometric titration of calcium ions by means of the zinc-phosphate electrode. The equivalence point lies at 1.89 ml of 0.1865 N K_3PO_4. 7.06 mg of Ca^{2+} was titrated with an error of 0.28%.

A sharp jump in potential is observed on adding 0.65 ml of K_3PO_4. The volume of potassium phosphate used for titration is designated by V_1.

2. To the second aliquot of test magnesium solution is added 2.4 mg of Mg^{2+}; this concentration of magnesium ions is designated by C_2 (second addition). The volume is made up to 25 ml again and the final solution titrated with potassium phosphate. A sharp jump in potential is observed at 1.3 ml of K_3PO_4 this time. The volume of K_3PO_4 used for titration is designated V_2. By substituting the results obtained in the formula

$$x = \frac{C_2V_1 - C_1V_2}{V_2 - V_1},$$

we find that x = 0.8 mg.

TABLE 1

Potentiometric Titration of Magnesium Solutions Using a Zinc-Phosphate Electrode

Normality of K_3PO_4 solution	Mg^{2+} taken for titration, mg	Mg^{2+} found, mg	Error in %
0.838	25.8	26.3	+1.93
	12.9	13.1	+1.54
	6.5	6.6	+1.66
	3.2	3.3	+3.12
0.419	25.8	26.0	+0.77
	12.9	13.0	+0.77
	6.5	6.4	−1.54
	3.2	3.3	+3.12
0.2095	25.8	25.7	−0.38
	12.9	12.8	−0.77
	6.5	6.7	+3.07
	3.2	3.3	+3.12
	1.6	1.7	+6.25
	0.8	0.9	+12,5

From Tables 2 and 3, it is clear that the maximum error by the double addition method does not exceed 3%, while the error obtained when the compensation method is not used amounts to 17%.

The application of the zinc-phosphate electrode for separate determination of calcium and magnesium, when these two are present simultaneously, was investigated. The solubility of magnesium phosphate is approximately 1000 times that of calcium phosphate:

$$\frac{S_{Mg_3(PO_4)_2}}{S_{Ca_3(PO_4)_2}} = \frac{7.6\cdot 10^{-4}}{7.1\cdot 10^{-7}} \approx 10^3.$$

The values of the solubility products $L_{sMg_3(PO_4)_2} = 2\cdot 10^{-23}$ and $L_{sCa_3(PO_4)_2} = 2\cdot 10^{-29}$ show that the less soluble $Ca_3(PO_4)_2$ will be precipitated first. It is known however, that solubility is not only determined by the value of L_s, but also by the type of salt [5]. If electrolytes participate in the reaction, in which the number of

TABLE 2

Potentiometric Determination of Magnesium by the Double Addition Method

Mg^{2+} taken, mg	Normality of K_3PO_4 solution	First addition of Mg^{2+}, mg	Vol. of K_3PO_4 used for titrating after first addition, ml	Second addition of Mg^{2+}, mg	Vol. of K_3PO_4 used for titrating after second addition, ml	Mg^{2+} found mg	Error in %
0.8	0.2095	0.8	0.65	2.4	1.30	0.8	0
1.6	0.2095	1.6	1.30	4.9	2.65	1.6	0
6.5	0.2095	6.4	5.00	19.4	10.05	6.5	0
3.2	0.838	3.3	0.65	9.6	1.28	3.2	0
6.5	0.838	6.4	1.28	19.4	2.58	6.4	—1.53
0.80	0.2095	2.4	1.30	3.2	6.25	0.80	0
1.60	0.2095	4.9	1.65	6.0	3.10	1.58	—1.25
3.20	0.2095	3.2	2.61	5.4	3.92	3.17	—0.94
0.80	0.2095	3.2	1.63	5.7	2.65	0.79	—1.25
1.60	0.2095	11.3	5.02	24.2	10.05	1.57	—1.87
3.20	0.2095	9.7	5.02	22.6	10.05	3.17	—0.94

TABLE 3

Potentiometric Determination of Calcium by the Double Addition Method

Ca^{2+} taken, mg	Normality of K_3PO_4 solution	First addition of Ca^{2+}, mg	Vol. of K_3PO_4 used for titrating after first addition, ml	Second addition of Ca^{2+}, mg	Vol. of K_3PO_4 used for titrating after second addition, ml	Ca^{2+} found, mg	Error in %
1.42	0.743	0.35	0.12	2.12	0.24	1.42	0
0.35	0.343	0.36	0.10	0.71	0.15	0.34	—2.85
0.71	0.343	0.35	0.15	0.71	0.20	0.73	+2.81

positively and negatively charged ions is not the same, the value of $\sqrt{L_s}$ does not directly indicate the order of precipitation of the salts. The direction taken by the reaction and the extent to which it proceeds are determined by K, which is the ratio of L_s for the precipitates participating in the reaction, raised to a power which is equal to the respective coefficients.

In our case, when

$$L_{sMg_3(PO_4)_2} = 2 \cdot 10^{-23} \text{ and } L_{sCa_3(PO_4)_2} = 2 \cdot 10^{-29},$$

$$\text{the value of } K = \frac{L_{sMg_3(PO_4)_2}}{L_{sCa_3(PO_4)_2}} = 10^6$$

and the reaction favors the less soluble phosphate. Using Tananaev's formula [6], $C = \frac{100 \cdot K}{K + 1}$, it is possible to calculate the extent to which the reaction goes in favor of the calcium phosphate:

$$C = \frac{10000 \cdot 100}{10000 + 1} = 100\%;$$

i.e., the reaction favors formation of calcium phosphate 100%. Tests completely confirmed this assumption. Calcium was first titrated and then the magnesium. The first jump occurred after deposition of all the calcium, while the second jump occurred after deposition of the magnesium (Fig. 3).

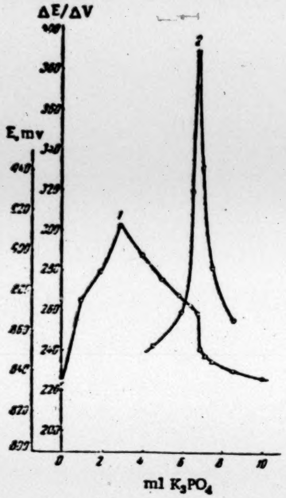

Fig. 3. Potentiometric titration of calcium and magnesium, when both are present, by means of a zinc-phosphate electrode. 1) First potential jump at 2.93 ml of 0.2523 N K_3PO_4. 14.83 mg of Ca^{2+} titrated with an error of +1.02%; 2) potential jump at 6.78 ml 0.2523 N K_3PO_4. 11.82 mg of Mg^{2+} titrated with an error of 1.00%.

The method of double additions is more rapid and simple than a method in which attempts are made to introduce corrections for the titration error.

Determination of calcium and magnesium when both are present simultaneously takes two hours; a normal gravimetric determination takes more than 24 hours.

SUMMARY

1. Calcium and magnesium which are present together in solution can be titrated with a solution of an alkali phosphate by using a zinc-phosphate electrode of the second kind.

2. It has been shown that it is possible to eliminate normal titration errors by carrying out titration by the method of double additions.

3. By means of the zinc-phosphate electrode it is possible to determine 35 mg/liter of Ca^{2+} with an accuracy of 0 to ± 2.81%, and 80 mg/liter of Mg^{2+} with an accuracy of 0 to ± 1.87%.

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SPECTROGRAPHIC DETERMINATION OF URANIUM IN ORES AND THE PRODUCTS OBTAINED BY TREATMENT OF THESE ORES

N. G. Morozova

Spectrographic determination of small amounts of uranium in ores is a special problem, since the sensitivity of detection of this element is low. The trouble is that uranium and its oxides are characterized by low volatility, and reduction of uranium to the metal and the evaporation of the metal proceed at high temperatures (the b.p. of uranium is about 3900°). Furthermore, uranium, like many other elements of the lanthanide and actinide groups which have several electrons in the incomplete 4f and 5f orbits, has a very complex spectrum with a large number of spectrum lines of low sensitivity.

The difficulties connected with the detection of small amounts of uranium partly explains the small number of publications devoted to spectrographic determination of this element. There are only two Russian publications on spectrographic determination of uranium in ores. The method described by Bogdanova, Moroshkina, and Prokofiev [1], permits determination of a thousandth and ten thousandth percent uranium in samples; all the same, the method is complicated, since it necessitates getting test samples into solution; uranium is then partly removed by ion-exchange on a cation exchange resin. The resin is fused into a bead whose uranium content is then determined by the method of additions. The second method has been briefly described in the review by Vinogradov [2]; this method is based on direct and complete combustion of test samples in the carbon electrodes of a dc, arc; exposure takes 7 minutes. By this method it is possible to determine 0.001% of uranium in a sample. Quantitative determinations can only be carried out at uranium concentrations of not less than 0.005%. Further, the large exposure time contributes an appreciable share to the duration of an analysis. The original technique adopted in the present work is the use of isotopic additions as internal standards; this technique reduces to a minimum the effect of third components and variations in experimental conditions.

Of numerous foreign papers on this subject, the method of Strasheim is worthy of attention [3]; in particular, his variant which consists of adding a "strengthening agent" is of interest; this technique makes it possible to increase the sensitivity of uranium detection to 0.006%. The author, however, notes that for uranium contents of less than 0.01%, the analytical line is not readily distinguishable from the background, thereby making quantitative determination difficult.

The method described below is based on direct determination of uranium in ores differing in composition, without preliminary chemical preparation for contents of 0.005% and higher.

1. Excitation of the Uranium Spectrum

As a result of the low ionization potential of uranium, which is approximately four electron volts, the lines of the once ionized atom are excited as well as those of the neutral atom in arc sources. Under these conditions, the sensitivity of the UI lines are appreciably lower than the U II lines. On the basis of orientating calculations for extent of ionization using the Sach formula, one could expect an appreciable increase in "arc" lines only at discharge temperatures below 4000° since, even at this temperature, percentage ionization amounts to about 75%. Low temperatures, however, are not favorable to evaporation of uranium and slightly volatile ore components, as a consequence of which the use of low temperature sources, e.g., a flame, is not expedient.

The sensitivity of U II lines decreases in spark sources, and in the hardest operating spark conditions, as well as in a low voltage impluse discharge (without inductance), a number of intense lines of ionized uranium appear [4]. Since the intensity of these lines decreases rapidly with an increase in the resistance of the discharge circuit, it is difficult to use them for determining uranium in ores which are characterized by low electrical conductivity.

Accordingly, it is expedient to use the sensitive lines in the spectrum of once-ionized uranium as analytical lines for determining uranium, and to excite the spectrum in an arc.

2. Experimental Technique

Two methods have been developed for determining uranium:

1) the bricketting method for samples containing more than 0.1% uranium;

2) combustion of test samples on copper electrodes for uranium concentrations of 0.005% and higher.

The PS-39 arc generator, stabilized by a resistance* and carefully adjusted, was used for exciting the spectra. Control of the stability of the generator was realized oscillographically. The spectra were photographed on a KS-55 spectrograph with glass lenses.

For the bricketting method, test sample was mixed with copper powder in the ratio of 1 : 9 in order to increase the electrical conductivity, and also with an internal standard, and pressed into a brickette by means of a hydraulic press at a pressure of 10^4 kg/cm^2. Pressing was carried out in a steel pressformer with two sided pressure, which ensured even density of the brickette with height [5].

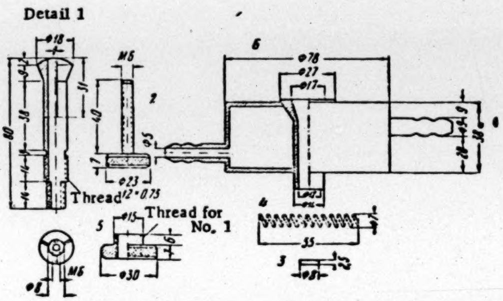

Fig. 1. Details of the brickette holder.

After testing several elements, the element chosen as an internal standard from a number of less volatile elements was molybdenum which was used as ammonium molybdate.

In order to improve the stability of the arc discharge on the brickette and to increase the reproducibility of determinations, a special brickette holder with water cooling was constructed. A sketch of the details of the brickette holder is given in Fig. 1, while a general view of the holder is given in Fig. 2. The brickette is placed in the opening of the tongs 1, provided with three grooves and, by means of screw 2 and washer 3 fitted with spring 4, placed within the tongs, is fixed so that its top end sticks out slightly. The brickette is then pressed onto the tongs with a flat disc, and tightened up with nut 5. Water is circulated through container 6 to cool the brickette and to prevent it from melting. The construction of the brickette holder enables one to switch brickettes rapidly, ensures that they are fixed at the correct height, and that they are uniformly cooled during arc operation.

The second method is very simple. Test sample is mixed with internal standard and closely packed into small holes drilled in a copper disc which serves as the lower electrode of the arc; the upper electrode is a "false" copper electrode. One of the characteristics of copper electrodes is that they are not heated to high temperatures, in contrast to carbon or graphite electrodes which are most often used for analyzing powdered materials. Consequently, there is no point in drilling deep grooves; the ratio of the diameter to the depth should be greater than one.

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* The resistance of 100,000 ohms and 10 watts was introduced in series in the secondary of the transformer.

During direct combustion of test samples in copper electrodes, it is possible to carry out quantitative determination of uranium on samples containing up to 0.01%. At concentrations of 0.01-0.02% however, the calibration curves have a greater slope, which decreases analytical accuracy. There is also a drop in sensitivity for uranium determination in certain ores and products obtained during their treatment. Limestones and certain types of production wastes belong to this class.

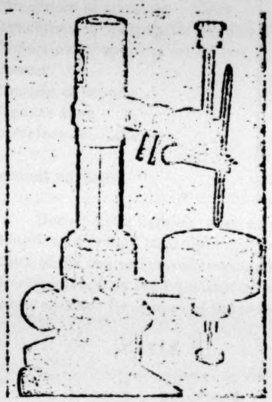

Fig. 2. General view of the brickette holder.

Sensitivity can be increased by pressing the samples beforehand into tablets (in contrast to brickettes, we call tablets those which are made without including copper powder for dilution). Similar results are obtained by fusing the tests into beads. Fusion can be carried out in carbon electrodes heated by a dc current or even by means of an evaporator [6]. Both pressing and fusion of test samples leads to an increase in the absolute intensity of the uranium lines, and to an increase in relative intensity as compared with the spectrum background. The amplifying factor which is equal to

$$\left(\frac{I_l - I_b}{I_b}\right)_{\substack{\text{beads}\\ \text{tablets}}} : \left(\frac{I_l - I_b}{I_b}\right)_{\text{powder}},$$

is approximately the same for tablets and beads, and varies roughly within the limits 1.5-2 for different samples. The sensitivity for uranium determination under these conditions is 0.005%.

In order to increase sensitivity of uranium determination in limestones, it is necessary before pressing test samples to dilute them with silica in a proportion of 1 : 1. Experimental conditions are given in Table 1.

3. Effect of the Bulk Composition of the Ore on Experimental Results of Uranium Determination

The use of spectroscopic methods for getting accurate quantitative results during analysis of ores is bound up with special difficulties which are determined by the variation in the chemical composition of test materials. The ore composition affects both the absolute intensity of the analytical lines as well as the relative intensity, since it is difficult to choose an element whose physicochemical properties are similar to those of the test element for comparing intensities.

In order to have an idea of the effect of the composition of the ore on uranium determination, a study was made of the relative intensity of the analytical pair of lines in the spectra of synthetic samples containing different amounts of the major ore components.

The basis of the synthetic samples was silica, which was mixed in various amounts with ferric oxide, magnesium oxide, alumina, calcium sulfate, and copper. The amount of uranium and inner standard added to each sample was the same for each sample. The mixtures were fired directly in an ac arc, or diluted with copper powder (1 : 9) and pressed into brickettes.

Results for measurements of the logarithm of the relative intensity of brickette spectra are given in Table 2. Every figure quoted is the mean of four spectrograms. The results obtained indicate that the relative intensity of the analytical pair of lines is independent of sample composition when the bricketting technique is used. The absence of any effect is no doubt connected with the appreciable dilution with copper powder. Only on switching to "pure copper" was there observed a change in the intensity of the analytical lines, since when this is done there is a change in the properties of the brickette, its thermal conductivity and electrical conductivity.

TABLE 1

Parameters	Bricketting method	Combustion of test samples in copper electrodes
Analytical lines	U II 4090 · 14 A and Mo 4086 · 025 A	
Photographic plates	Spectrographic, type II, sensitivity II, GOST Units	
Spectrograph slit width	0.02 mm	
Upper electrode	Copper rods shaped to a cone with chamfered end	
Dimensions of brickette - tablet	Diameter 8 mm, height 4-6 mm;	Diameter 4 mm, height 2 mm
Dimensions of openings for powders		Diameter 3 mm, depth 2 mm
Dimensions of openings for tablets		Diameter 4 mm, depth 2 mm
Current	6 a	8 a
Duration of heating	20 seconds	
Exposure time	40 seconds	40 seconds
Interelectrode distance	2.5 mm	2.5 mm
Internal standard	4% ammonium molybdate	0.5 or 1% ammonium molybdate

During direct burning, when no dilution is used, the relative intensity of the analytical lines depends in a complicated fashion on sample composition (Fig. 3). In the more complicated three component mixtures, the effect of the composition decreases somewhat. In Fig. 4, as an illustration, a comparison is made of the curves showing changes in the logarithm of relative intensity for spectra obtained with silica and alumina, and similar curves obtained for spectra of the same mixtures to which 20% ferric oxide has been added.

TABLE 2

	Silica in %	100	90	75	50	25	0
	Amount added in %	0	10	25	50	75	100
Additives	Ferric oxide	0.05	0.04	0.04	0.05	0.04	0.045
	Alumina	0.05	0.04	0.06	0.05	0.05	0.04
	Magnesium oxide	0.04	0.05	0.03	0.04	0.04	0.05
	Calcium sulfate	0.04	0.04	0.03	0.06	0.06	0.05
	Copper	0.05	0.04	0.045	0.05	0.08	0.14

Synthetic mixtures, of course, do not fully reflect the behavior of ores which contain various impurities at different concentrations. In order to find out how variations in the composition of natural materials can affect uranium determination, samples of ores were chosen which contained the smallest amounts of iron, calcium, magnesium and aluminum. These elements were added to test samples in amounts which were 15% by weight of the test (Table 3).

It was established that such additions, with the exception of iron, do not affect the relative intensity of the analytical pair of lines. The presence of iron depresses the relative intensity of the analytical lines to some extent.

4. Calibration Curves

Determination of uranium in ores of differing composition by the bricketting technique can be carried out on the basis of a common calibration curve constructed by means of synthetic standards. The standards were prepared by successive dilution of uranoso uranic oxide with silica. 4% of ammonium molybdate and 9 parts of copper powder were added to each standard. Standards were also prepared for comparison on the basis of an ore which had been chemically analyzed for its uranium content. Results for construction of calibration curves are given in Table 4.

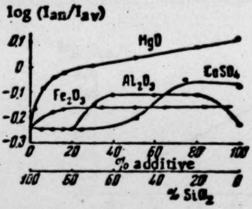

Fig. 3. Effect of composition on relative intensity of the analytical lines.

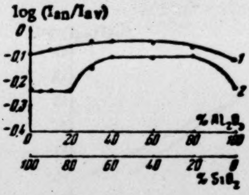

Fig. 4. Effect of composition on relative intensity of analytical lines: 1) mixture of $SiO_2 - Al_2O_3$ with 20% Fe_2O_3; 2) mixture of SiO_2 and Al_2O_3.

TABLE 3

Composition of sample	SiO_2	MgO	Fe_2O_3	CaO	K + Na	MnO_2	Al_2O_3	Log of relative intensity
Ore (no additives)	71.5	0.58	3.5	1.9	2.7	0.18	—	—0.05
Ore + 15% MgO	71.5	15.58	3.5	1.9	2.7	0.18	—	—0.04
Ore + 15% Fe_2O_3	71.5	0.58	18.5	1.9	2.7	0.18	—	—0.08
Ore + 15% $CaSO_4$	71.5	0.58	3.5	8.0	2.7	0.18	—	—0.045
Ore + 15% Al_2O_3	71.5	0.58	3.5	1.9	2.7	0.18	15.0	—0.05

TABLE 4

Standards prepared from ore		Standards based on silica	
uranium concentration	log of relative intensity	uranium concentration	log of relative intensity
—	—	0.10	—0.335
—	—	0.16	—0.22
0.26	—0.108	0.25	—0.11
0.50	+0.058	0.50	+0.05
0.80	+0.17	0.80	+0.16

Table 4 shows that, within the limits of experimental accuracy, the standards based on different materials give a common calibration curve No. 1 which is shown in Fig. 5. Further, this same curve is obtained when standards are used which had been made from other materials; alumina, magnesium, iron, and calcium sulfate.

For determination of uranium by the method of direct combustion of samples, it is only possible to use the common calibration curve for ores similar in composition, e.g., silicate ores of various origins, containing 50-70% silica.

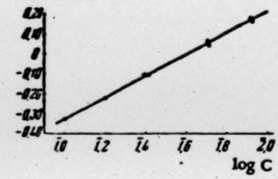

Fig. 5. Calibration curve for determining uranium by the bricketting method: •) synthetic standards; o) standards made from a natural ore.

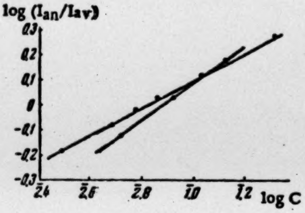

Fig. 6. Calibration curves for determining uranium by direct combustion of test samples.

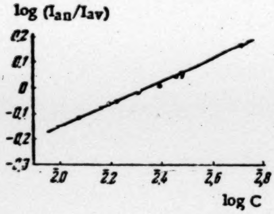

Fig. 7. Calibration curve for determining uranium by pressing ores into tablets: •) standards based on ore 1; o) standards based on ore 2; x) standards based on ore 3.

Standards were prepared from ore samples containing a small amount of uranium, which had been accurately established by control chemical analysis. Increasing uranium concentrations were obtained by adding known amounts of U_3O_8 to these samples.

In Fig. 6 is shown the calibration curve for determining uranium in ores which contain 50-70% silica (Curve No. 2) or 30-40% ferric oxide (Curve No. 3). It is possible, by means of Curve 2, to analyze limestones, as long as test samples are diluted with silica in the proportion of 1 : 1.

The deviation between curves 2 and 3 increases towards low concentrations, and becomes large enough to lead to incorrect results if one of them is used for analyzing any ore. When pressed samples (tablets) or beads are used such a deviation is not observed. In this case, the common calibration curve No. 4 shown in Fig. 7, constructed on the basis of standards made from ores of different composition, is obtained. The composition of the ores is given in Table 5.

TABLE 5

Sample number	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	MnO
1	71.5	3.0	—	6.7	1.1	0.05
2	61.9	10.0	22.6	3.6	1.1	—
3	48.4	31.7	11.8	1.6	4.4	0.6

5. Accuracy and Reproducibility of Results

The main sources of error in determining uranium in ores are variation in light source, its screening by the edge of the lower electrode, and innacurate determination of the contrast coefficient of the photographic plate.

The particle size of the mixed powders is also of essential importance.

The reproducibility of uranium determination by the bricketting technique, and by the method of firing the samples in copper electrodes, was found to be characterized by a probable error for a single determination of ± 5%, on the basis of 100 spectrograms. The bricketting method gives high results at high manganese concentrations (8% MnO_2) of the samples, and for uranium determination in the concentration range 0.1–0.15 when the iron content exceeds 20% as Fe_2O_3.

TABLE 6

Sample number	Bricketting method			Sample number	Method of combustion of samples in copper electrodes		
	spectrographic	chemical			spectrographic	chemical	
		I	II			I	II
1	0.54	0.54	0.54	1	0.048	0.048	0.040
2	0.275	0.308	0.31	2	0.072	0.070	0.059
3	0.66	0.65	0.67	3	0.058	0.059	0.06
4	0.26	0.28	0.23	4	0.073	0.073	0.07
5	0.36	0.36	0.305	5	0.21	—	0.21
6	0.175	0.17	0.156	6	0.035	—	0.038
7	0.26	0.26	0.22	7	0.052	—	0.05
8	0.30	0.34	0.26	8	0.12	—	0.12
9	0.21	0.24	0.15	9	0.068	—	0.07
10	0.17	—	0.16	10	0.028	0.032	0.028
11	0.125	—	0.12	11	0.035	0.033	0.031
12	0.215	—	0.21	12	0.032	0.032	0.026
13	0.18	—	0.17	13	0.030	0.029	0.028
14	0.60	0.61	—	14	0.034	0.034	0.032
15	0.34	0.345	—	15	0.021	0.022	0.016
16	0.26	0.24	—	16	0.030	0.031	0.030
17	0.22	0.212	—	17	0.028	0.030	0.028
18	0.125	0.13	—	18	0.022	0.022	0.019

The agreement between the results of spectrographic determinations and chemical analysis, carried out in two laboratories, are illustrated by the figures given in Table 6. Chemical analysis which is taken as the control, and designated by the number 1, was carried out with particular care.

In most cases fairly satisfactory agreement was reached between the results of chemical and spectrographic analysis. The suggested spectrographic methods of determining uranium, in addition to possessing satisfactory accuracy, are much more rapid and the technique itself is simpler than chemical methods, and they can be used for analyzing ores of differing composition.

This work was carried out with the cooperation of students of Leningrad State University. Professors V. K. Prokofiev and K. I. Taganov gave it their constant attention, for which I am very grateful.

SUMMARY

1. Methods for the determination of uranium in the direct current arc with copper electrodes are described. The determination is carried out by the direct burning of samples (for contents > 0.2 % of uranium) or after brickette samples diluted 10 times with copper powder (for contents > 0.1% of uranium). For stabilizing the arc discharge the brickettes are cooled in a special brickette holder.

The probable error of a single determination in both cases is ± 5%.

2. It has been recommended that samples be pressed or melted before analysis (without any additional dilution) in order to raise the sensitivity of the uranium detection (~ to 0.005%).

3. In the brickette method the results do not depend on the composition of a sample and different samples can be analyzed by the common calibration curve. In the method of the direct burning of samples the use of the common curve is possible with the ores of similar composition.

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• See C. B. Translation.

DETERMINATION OF CHROMIUM BY MEANS OF PERCHLORIC ACID IN THE PRESENCE OF MANGANESE DIOXIDE AS CATALYST

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A method has been published for the determination of chromium in which the latter is oxidized to the sexivalent state by means of perchloric acid [1,2]. In those cases where chromium is found in ores, rocks, and sparingly soluble alloys, it is necessary to dissolve test samples beforehand in a mixture of sulfuric and perchloric acids [3]. All the same, according to certain results, in the presence of sulfuric acid Cr^{3+} is not completely oxidized to Cr^{VI}, as a result of which low results are obtained [4]. The aim of the work described here was to establish the conditions necessary to ensure complete oxidation of chromium by perchloric acid in sulfuric acid media.

First to be studied was the effect of sulfuric acid concentration on completeness of oxidation of chromium under the following conditions. Into a 100 ml conical flask was introduced an aliquot of sample containing a known amount of chromium; 20 ml of sulfuric acid of varying concentrations was then added, and this followed by 2 ml of 40% perchloric acid. The contents of the flask were then heated till solution of sample was complete. Boiling was continued for another two minutes after the sample had dissolved completely, and the flask and contents then cooled. 50 ml of water was added and the solution boiled to removed all traces of chlorine. The amount of sexivalent chromium was determined by reducing it with excess Mohr's salt, the latter being then back titrated with potassium permanganate.

TABLE 1

Sp. gr. sulfuric acid d_4^{25}	Chromium found	
	in mg	in %
1.56	100.5	64.8
1.42	111.3	71.8
1.28	122.5	79.0
1.17	136.0	87.7
1.09	141.0	91.0

From the results obtained (Table 1), it is clear that sulfuric acid concentration has an essential affect on the extent to which chromium is oxidized by perchloric acid. The amount of chromium oxidized increases with decreasing sulfuric acid concentration. At high acidities of the solution, there was observed a reverse reduction of the chromate ion during oxidation, and the orange color of the solution turned back again into green. This, presumably, can be explained by the fact that under certain conditions perchloric acid may decompose to form hydrogen peroxide according to the equation:

$$2HClO_4 \rightarrow H_2O_2 + Cl_2 + 3O_2$$

which converts the chromate ion into perchromic acid. The latter readily decomposes to form compounds of trivalent chromium, as a consequence of which complete oxidation of chromium during analysis is not achieved in the final count. Formation of perchromic acid during incomplete oxidation of chromium by perchloric acid is confirmed by the transition of the orange color of the solution to blue, and then to green, which is observed on shaking the liquid with ether or benzene. This was also observed during oxidation of chromates by hydrogen peroxide in sulfuric acid solution [5].

In order to get a more accurate picture of the effect of hydrogen peroxide on the oxidation of chromium by perchromic acid, we carried out some determinations of chromium in the presence 1 ml of 30% hydrogen peroxide solution added on purpose. Oxidation was carried out at the optimum sulfuric acid concentration of d_4^{15} 1.08.

Results of these experiments are given in Table 2.

TABLE 2

Chromium taken in mg	Cr found in mg		Cr found in %	
	without H_2O_2 added	with H_2O_2 added	without H_2O_2 added	with H_2O_2 added
31.0	27.2	5.3	87.7	17.1
	27.1	5.0	87.4	16.1
30.6	28.3	5.5	92.5	18.0
	28.5	5.4	93.1	17.6

Percentage reduction of sexivalent chromium also depends on duration of oxidation and temperature (Tables 3 and 4).

As can be seen from Tables 3 and 4, increasing duration of oxidation and raising the temperature at which oxidation is carried out lead to a decrease in percentage oxidation of chromium as a result of reduction of sexivalent chromium.

TABLE 3

(62.0 mg Cr taken)

Duration of oxidation in minutes	Found	
	in mg	in %
2	56.6	91.3
3	56.1	90.5
7	23.2	37.4
12	21.1	34.0

TABLE 4

(92.0 mg Cr taken)

Temperature in °C	Cr found	
	in mg	in %
200	84.9	92.3
205	74.1	80.5
210	66.9	72.7
225	60.3	65.6

In order to oxidize chromium with perchloric acid at as low a temperature as possible in the minimum possible time, we used manganese dioxide as catalyst. Results for determination of chromium by oxidation with perchloric acid in sulfuric acid media, using 0.2 g of manganese dioxide as catalyst, are given in Table 5.

TABLE 5

(153.0 mg Cr taken)

Temperature in °C	Time in minutes	Cr found in mg		Cr found in %	
		without catalyst	with catalyst	without catalyst	with catalyst
130	2	10.2	148.2	6.7	97.0
170	2	21.5	150.5	14.0	98.4
180	2	21.6	152.0	14.1	99.4

As the results given in Table 5 show, complete oxidation of chromium is achieved in the presence of manganese dioxide at relatively low temperatures (170-180°) in the course of the short time of 2 minutes. Using this technique, the color of the solution during oxidation does not turn the blue-green which is indicative of reverse reduction of chromium.

When determinations are carried out in the presence of manganese dioxide, the solution is filtered free from suspended particles of the catalyst prior to titration.

A. A. Apenkina took part in the work.

SUMMARY

1. When chromium is oxidized by means of perchloric acid in sulfuric acid media without using a catalyst, Cr^{3+} is not completely oxidized to Cr^{VI}.

2. Increasing reaction temperature favors reverse reduction of Cr^{VI} to Cr^{3+}.

3. In the presence of manganese dioxide as catalyst, oxidation of chromium by perchloric acid in sulfuric acid media proceeds at considerably lower temperatures, thanks to which the reverse reduction of Cr^{VI} to Cr^{3+} does not occur.

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CONDITIONS FOR THE PHOTOMETRIC DETERMINATION OF ARSENIC AS BLUE ARSENOMOLYBDIC ACID

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Photometric determination of arsenic on the basis of reduction of arsenomolybdic heteropolyacid to the "blue acid" [1-4] has certain essential drawbacks. Experiments have shown that systematic and relatively constant loss of arsenic is observed, particularly when small amounts of the latter are being determined. This fact limits the possibility of measuring the optical density of colored solutions by the comparison method alone. The following problems were the object of the work described here:

1) to find the reason for loss of arsenic, and to eliminate the factor causing this loss so as to increase the accuracy of the method;

2) to establish conditions which will ensure that a solution of blue arsenomolybdic acid which is stable with time, and is readily reproducible, is obtained.

All stages of the analysis were subjected to systematic study. Tests showed that the operation of decomposing metals and ores – both sulfide and oxides – in acid-oxidizing media is not accompanied by losses of arsenic. The subsequent operation, however – distillation of arsenic chloride into water – is accompanied by loss of arsenic irrespective of the composition of test material [5], and of the composition of the atmosphere under which the distillation is carried out [1,3].

In order to find out the reason for this loss of arsenic, an aliquot of iron ore which itself did not contain arsenic was taken through all the stages of the analysis, with a known amount of arsenic in the form of arsenite solution. The results obtained were then compared with those obtained by direct conversion of the same amount of arsenite into arsenomolybdic acid and reduction of it to the blue heteropolycomplex.

Measures directed towards improving trapping of the arsenic chloride by water, such as increasing the water column, cooling the water, decreasing the distillation rate, were unsuccessful.

As can be seen from Table 1, positive results were obtained on using an oxidizing agent as absorbent liquid – best of all hydrogen peroxide.

Losses during distillation into water are determined by the fact that the process of solution of arsenic chloride – which has the properties of the acid chloride of arsenous acid – in water is an equilibrium process:

$$AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$$

Equilibrium is shifted towards the left in the presence of high concentrations of hydrogen chloride and hydrogen bromide, which accompany arsenic chloride during distillation; the latter, under these conditions partly volatilizes from the aqueous solution. In an oxidizing medium arsenic acid is formed, which shifts the equilibrium to the right.

Nitric acid is less suitable then hydrogen peroxide as absorbent liquid, probably on account of the high vapor pressure of the gases formed during interaction of nitric acid with distilled hydrogen chloride.

The results given in Table 1, as well as long experience in ore analysis, indicate that there is no need to distill arsenic chloride in an inert gas atmosphere (N_2, CO_2), since quantitative and rapid distillation of arsenic is achieved by distilling with the azeotrope of $HCl + H_2O$, as long as the concentration of HCl in the original solution is not less than 15% by weight.

TABLE 1

Absorption of Arsenic By Various Media

mg of As taken for distillation with 1 g of ore C,O,3-a	As found in mg after distillation		
	in water	in HNO_3 (sp.gr. 1.4)	in H_2O_2 (1% solution)
1.0	0.84: 0.88: 0.87: 0,92	0.90: 0.91: 0.93: 0.88	0.96: 1.02: 1.01: 0.98: 1,02
0.5	0.38: 0.42: 0.46: 0,43	0.40: 0.45: 0.39	0.48: 0.50: 0.51: 0.48: 0,51
0.2	0.16: 0.16: 0.17: 0,16	0.19: 0.18: 0.20: 0.21	0.19: 0.19: 0.20: 0.21: 0,20
0.1	0.06: 0.08: 0.07: 0,06	0.08: 0.09: 0.08	0.10: 0.09: 0.10: 0.10: 0,11
0.05	0.03: 0.04: 0.03: 0,03	0.05: 0.04: 0.06: 0,05	0.014: 0.05: 0.05: 0.05: 0,04
0.03	0.02: 0.01: 0.02: 0.015	0.03: 0.03: 0.02	0.03: 0.025: 0.03: 0.035: 0.03

Of a number of materials tested as reducing agent, the most suitable was hydrazine sulfate in sulfuric acid, even in the absence of chloride. The slow reducing action of hydrazine sulfate, which is manifested only on heating, favors formation of very stable solutions of the blue acid. The optical density of these solutions remained unchanged for 40 days for 0.005 - 0.1 mg of arsenic in 50 ml solution. In the presence of sodium chloride, the stability and reproducibility of the optical density of the solutions deteriorate, there being a certain increase in its absolute value.

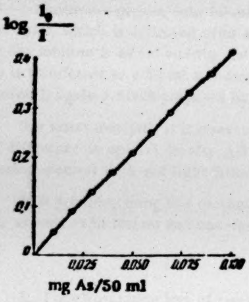
At appreciable concentrations of ammonium chloride, the optical density decreases essentially. All salts restrain development of the color of the solutions.

For these reasons, it is better to remove hydrochloric acid by evaporating the distillate to dryness rather than by neutralizing it [3, 6].

At arsenic concentrations greater than 0.1 mg in 50 ml of solution, the optical density of the solutions shows poor reproducibility, while with a drop of concentration to below 0.005 mg As in 50 ml of solution, the reduction reaction slows down considerably and does not proceed to completion. Thus, the concentration limits which can be determined are established, not on the basis of the thresholds of sensitivity of the reaction and on the resolving capacity of the optical apparatus, but on the conditions of formation of the colored solution.

The acidity of the solution to be measured colorimetrically should be within the limits of 0.1 - 0.5 N. At lower sulfuric acid concentrations, excess molybdate which has not been complexed reacts, while at the same time silica is extracted from the glass. At higher acidities, color intensity weakens, and both the stability and reproducibility of the optical density of the solutions deteriorate. The use of stronger reducing agents such as stannous chloride and ascorbic acid, even in the cold, leads to rapid formation of a blue solution whose optical density is stable for 1.5-2 hours and is reproducible only within a narrow arsenic concentration range; the upper limit is scarcely 0.03-0.04 mg in 50 ml.

In the dry residue, on evaporation, the distillate of arsenic acid is covered with salts, mainly silicates leached out of the glass. The salt film hinders solution of the arsenic acid in water even on prolonged boiling; only by successive treatment of the dry residue with the minimum amount of alkali, followed by hot water, is the arsenic rapidly and completely brought into solution. It is clear from the diagram that the solutions obtained under the conditions described obey Beer's law satisfactorily.



Calibration curve
(20 mm cell; red light-filter 680–700 mμ).

Determination of Arsenic in Ores and Metals

0.5 - 1 g of sample is dissolved in 10 ml of a mixture of concentrated nitric and hydrochloric acids in the proportion 1 : 3, by heating in a beaker; or, depending on the type of material, the sample can be treated successively with these two acids. 10 ml of sulfuric acid (1 : 1) is then added and, if necessary, hydrogen fluoride, and the whole evaporated the appearance of white fumes. (the beaker walls are washed with water and the contents again evaporated to white fumes. The contents of the flask are transferred to a long-necked round-bottom flask, the walls of the beaker are washed with hydrochloric acid (sp.gr. 1.12) and the volume made up to 50 ml with this same acid. 0.5 g each of hydrazine sulfate and potassium bromide are introduced and the mixture distilled; about 3/4 of the volume is distilled off until the residue is of a syrupy consistency. The arsenic is trapped in a beaker containing 10 ml of 1% hydrogen peroxide. 10 ml of nitric acid (sp.gr. 1.4) is added to the distillate which is then evaporated to dryness. The dry residue is moistened with 1-2 drops of 10% alkali solution; 25-30 ml of water is added, and the whole boiled for 3-5 minutes. The solution is cooled, and transferred to a 100 ml standard flask where it is made up to the mark with distilled water free from reducing agents (if necessary, the water should be treated with dilute permanganate). 10 ml of solution* is pipetted into a small beaker to which is then added 4 ml of reagent solution** and the volume made up to 40 ml; this final solution is heated to boiling and kept there for 3-5 minutes. On cooling, the solution is transferred to a 50 ml standard flask; the volume is made up to the mark with water and the color developed measured; the null solution used is a blank taken through all the analytical stages.

TABLE 2

Comparative Results for the Determination of Arsenic in Ores and Ferrous Metals

Test material	Arsenic found, in %	
	by the photo-colorimetric method	bromatometric method
Iron ore C.O. 2 (0.13% As)	0.12; 0.13	0.11
Manganese ore C.O. 44 (0.004% As)	0.003; 0.004	—
Cast iron, C.O. 57 (0.12% As)	0.12; 0.12	0.12
Steel, C.O. 58 (0.166% As)	0.154; 0.160	0.14
Polymetallic ore	0.38; 0.38	0.37
• •	1.66; 1.66	0.57
• •	0.29; 0.29	0.28
• •	3.78; 3.30	3.60

The reagents used should be free from arsenic: this can be checked by the absence of color in the blank. When the FEK-M instrument is used, the light filter KS-14 should be employed in conjunction with a cell whose thickness is 20 mm.

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* If the expected arsenic content is less than 0.005 % then 50 ml is pipetted, while for contents of the order of 0.1%, only 5 ml of solution is used.

** The reagent is prepared by mixing 50 ml of 1% ammonium molybdate solution in 6 N sulfuric acid with 5 ml of 0.15% hydrazine sulfate solution, and diluting with water to 100 ml.

The calibration curve is constructed by means of standard arsenite solution. Standard arsenite solution containing 0.01 mg As/ml is measured out in lots ranging from 0.5 to 10 ml. by means of checked Mohr pipetes and semimicro-burets, into 50 ml standard flasks. AsO_3^{3-} is oxidized with 0.02 N permanganate to a stable blue color, which is destroyed after a few minutes by dropwise addition of 0.15% hydrazine sulfate. 4 ml of reagent solution is added and the volume made up to 40 ml.; this solution is boiled for 3-5 minutes. The solution is transferred to a 50 ml standard flask, it is then diluted with water to the mark and mixed. The null solution is again a blank prepared by using all the reagents.

For series analysis, it is convenient to use tables with columns of: weight, percentage, optical density, and difference in optical density ΔD per 0.001% arsenic. The value of ΔD is equal to $(5-4) \cdot 10^{-3}$, while, by using spectral dark-red light filter (700 mμ), it can be increased to $8 \cdot 10^{-3}$.

It is possible, using this method, to determine from 0.0005 to 0.5% arsenic in polymetallic and iron ores, as well as in ferrous and non-ferrous metals.

SUMMARY

1. For eliminating loss of arsenic when determining small amounts of it, it is essential that:

a) the distillate which consists of a mixture of $AsCl_3$, HCl, HBr, and H_2O, should be trapped with hydrogen peroxide solution;

b) after evaporating the distillate to dryness, the dry residue containing arsenic acid should be dissolved in the minimum amount of alkali.

2. Rapid quantitative distillation of arsenic chloride from hydrochloric acid solution can be realized without passing an inert gas through the solution, as long as the concentration of hydrogen chloride in the original solution is not less than 15% by weight.

3. Solutions of the blue heteropoly complex obtained by reduction of arsenomolybdic acid with hydrazine sulfate in sulfuric acid media, posses high stability and reproducibility, even for an insignificant salt contration. The optical density of such solutions, within the limits of 0.005 - 0.1 mg. As in 50 ml, does not change over periods of more than a month.

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USE OF A DIVALENT CHROMIUM SOLUTION FOR DETERMINATION OF ANTIMONY

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Gravimetric, electro-analytical, titrimetric and other methods are known for determination of antimony. Determination of antimony by gravimetric methods reduces to preparation and weighing of Sb_2S_3 [1, 2], Sb_2O_4 [2], $(C_9H_6ON)_3Sb$ [3]. Determination of antimony as the quadrioxide is based on transformation of Sb_2S_5 into Sb_2O_4 at 750-800°. At higher temperatures there is a possibility of reduction of the quadrioxide to the volatile trioxide. The method in which antimony is precipitated by hydroxyquinoline as $(C_9H_6ON)_3Sb$ gives good results. Gravimetric methods of determining antimony are time consuming. One of the drawbacks of the electro-analytical method is the difficulty of getting a really close packed adhesive deposit on the cathode. It has been recommended that the platinum beaker (the cathode) be covered with copper [4]. It has been demonstrated that it is possible to use pure platinum as a cathode [5]. One of the fundamental conditions for depositing antimony from solutions of thio salts is removal of polysulfides which act as oxidizing agents of antimony. The electro-analytical method is not so accurate as the gravimetric method and requires a lot of time. Of the titrimetric methods, the ones normally used are: iodometric (Fe^{3+} and As^{3+} interfere); bromatometric [6-8] (possible in the absence of Cu^{2+}, Fe^{2+}, and As^{3+}); and the permanganometric method [6, 9] (Fe^{2+} and As^{3+} interfere). Solutions of titanous chloride and divalent chromium [10], have been used as reagent-reducing agents for potentiometric titration. Potassium dichromate, the sulfate of quadrivalent cerium and potassium bromate [10], have been used as oxidizing agents during potentiometric titration of antimony. The potentiometric determination of antimony gives good results.

Small amounts of anitmony can be determined photometrically as a complex with a yellow color $K[SbI_4]$ [11-13], and by means of methyl violet [14, 15], which, in acid solution gives with $SbCl_6^-$ a violet color. Determination of antimony by the iodide-pyridine method [16] is based on formation of the insoluble iodide-pyridine complex $PyHISbI_4$ which has a yellow color. Chlorides, bismuth, lead, trivalent arsenic, and silver interfere with this determination of antimony. The sensitivity of the method is 0.05 mg Sb in 50 ml of final volume. Arsenic, cerium, iron, thallium, tin, etc., interfere with photometric determination of antimony by means of tetraethylrhodamine.

We have used a solution of divalent chromium for determining Sb^V and Sb^{III}. Preliminary experiments showed that pentavalent antimony is quantitatively reduced by Cr^{2+} ions to metallic antimony in neutral or weakly acid media. No ions of Sb^V and Sb^{III} are left in solution after removal of the precipitate. The black deposit of metallic antimony separates out in the cold. Under these conditions, arsenic remains in solution.

The filtered precipitate was washed with 2% ammonium chloride and brought into solution by addition of oxidizing agent, excess of which was determined titrimetrically. The use of a standard solution of potassium permanganate – excess of which was titrated with oxalic acid – as oxidizing agent did not give positive results. A weaker oxidizing agent – potassium dichromate – was used. The precipitate of elemental antimony was titrated with 0.20 N $K_2Cr_2O_7$ in the presence of 20 ml H_2SO_4 (1 : 4); excess dichromate was titrated with Mohr's salt in the presence of diphenylamine. Under these conditions, during determination of 24.6 mg of Sb, the following values were obtained 22.2; 22.2; 24.1; 22.7; 22.2; 22.2 mg Sb.

Satisfactory results were obtained under the following conditions. After oxidation of antimony by standard potassium dichromate solution excess of the latter was reduced with a solution of Mohr's salt, (the solution of Mohr's salt was added in excess), and the final solution titrated with potassium dichromate in the presence of diphenylamine; the volume of H_2SO_4 (1 : 4) was 20 ml. For lowering the potential of the system Fe^{3+}/Fe^{2+}, and getting a clear cut change in indicator color, phosporic acid was added to complex the Fe^{3+}. When diphenylamine is used it is necessary to introduce a correction for each determination. For comparison, results obtained by the gravimetric method of Wortman and Metsel for antimony are also included [2].

During oxidation of metallic antimony with a standard solution of potassium dichromate, excess of which was determined by titration with a solution of Mohr's salt in the presence of phenylanthranilic acid, the following results were obtained (Table 2).

TABLE 1

Sb found, in mg	
Gravimetrically	After reduction with divalent chromium
27.82	27.52
25.95	25.94
30.53	30.56
27.82	27.03
27.82	27.03

TABLE 2

Sb found, mg	
Gravimetrically	After reduction with divalent chromium
30.53	31.29
27.82	27.76
25.95	25.30

Titration error with phenylanthranilic acid is less than with diphenylamine. Thus, by using phenylanthranilic acid as indicator, it is possible to titrate excess $K_2Cr_2O_7$ directly with Mohr salt solution. When phenylanthranilic acid is used, there is no need to add phosphoric acid.

When diphenylamine is used, best results are obtained by reducing excess potassium dichromate with a standard solution of Mohr's salt, excess of the latter being titrated with potassium dichromate in the presence of phosphoric acid.

Satisfactory results were obtained for the determination of small amounts of antimony when a solution of divalent chromium was used (Table 3).

We established that 0.01 N potassium dichromate only oxidized metallic antimony to Sb^{3+}; acidity and duration of the reaction does not affect the extent of the oxidation.

To oxidize metallic antimony (0.2 - 0.05 mg) to the pentavalent state, it is necessary to use 0.1 N $K_2Cr_2O_7$.

Divalent chromium will reduced antimony ions (Sb^V and Sb^{III}) to the elemental state at antimony concentrations of 0.05 mg in 100 ml of final solution. A determination takes 10 minutes.

We recommend the following procedure for determination of antimony by means of divalent chromium solution.

The solution, containing pentavalent antimony ions is diluted with distilled water to a volume of 100 ml, and is neutralized to give a neutral or weakly acid medium (using ethyl range as indicator), Cr^{2+} solution is added and the whole is heated. The precipitate of metallic antimony is washed on the filter with 2% ammonium chloride solution 2-3 times. The precipitate is then transferred to the titration flask, it is acidified with sulfuric acid 1 : 4 (20 ml), and standard potassium dichromate solution added. After 5-10 minutes, the solution is titrated with a solution of Mohr's salt to a weak yellow color, 6 drops of phenylanthranilic acid indicator solution is added, and titration carried through till the color change.

The gram-equivalent of antimony is a fifth of the atomic weight.

One can also transfer the filtered and washed precipitate of antimony to the titration flask, and add H_2SO_4 1 : 4 (20 ml), followed by a known volume of $K_2Cr_2O_7$. After 5-10 minutes, excess of a standard solution of Mohr's salt is added, and the resultant solution titrated with potassium dichromate; near the equivalence point, phosphoric acid (3-5 ml) and diphenylamine are added. Titration is complete when a blue color appears.

The Cr^{2+} solution can be prepared either by the author's method [18, 19] or by Popov's method [17].

TABLE 3

Sb taken, in mg	Sb found, in mg	Observations	Sb taken, in mg	Sb found, in mg	Observations
5.00	5.50	1. Diphenylamine indicator	1.00	0.97	1. Phenylanthranilic acid indicator
5.00	4.60	2. 0.2 N $K_2Cr_2O_7$	1.00	0.97	
5.00	4.90		1.00	0.97	
5.00	5.00	3. pH of solution during reduction of antimony: 6.2-7	1.00	0.97	2. 0.1 *N* $K_2Cr_2O_7$ 0.01 *N* $K_2Cr_2O_7$
3.00	2.70		1.00	1.07	
3.00	2.90		0.20	0.20	
3.00	3.10		0.20	0.20	3. pH 6.2—7
3.00	2.80		0.20	0.20	4. H_2SO_4 1 : 4 (5—10 ml
2.00	1.80	4. Final volume of solution: 100-200 ml	0.20	0.20	
2.00	1.95		0.20	0.20	5. Final volume of solu- during reduction of antimony
2.00	1.95		0.05	0.05	
2.00	2.00		0.05	0.05	
1.00	0.93	5. H_2SO_4 1 : 4	0.05	0.05	
1.00	1.07	20-10 ml	0.05	0.05	60—100 ml

The advantages of the method just described, in which Cr^{2+} is used for determining antimony, over other methods, are: a) rapidity; b) possibility of determining antimony in the presence of arsenic.

SUMMARY

1. Cr^{2+} ions quantitatively reduce Sb^V to metallic antimony from neutral or weakly acid solutions. Under these conditions, arsenic is not reduced to the elemental state.

2. Metallic antimony is oxidized in the presence of sulfuric acid by means of a standard solution of $K_2Cr_2O_7$. Excess $K_2Cr_2O_7$ is determined by titration with a solution of Mohr's salt, using phenylanthranilic acid as indicator.

3. During the use of diphenylamine as indicator, best results are obtained when, after dissolving the metallic antimony in standard $K_2Cr_2O_7$ solution (in sulfuric acid solution), a solution of Mohr's salt is added, and excess of the latter titrated with $K_2Cr_2O_7$ in the presence of phosphoric acid.

4. It has been established that it is best to use 0.2 N $K_2Cr_2O_7$ for antimony contents up to 1 mg. For lower concentrations of antimony, 0.1 N $K_2Cr_2O_7$ should be used.

5. Tri- and pentavalent arsenic do not interfere.

6. The sensitivity of the method is 0.05 mg of Sb in 100 ml solution.

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* See C. B. Translation.

THE USE OF β-FURFURALDOXIME FOR DETERMINING LARGE AMOUNTS OF PALLADIUM IN THE PRESENCE OF COPPER AND NICKEL

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In 1928 Ephraim [1] first suggested the use of salicylaldoxime for the detection and gravimetric determination of copper. Later, this reagent was used for the quantitative determination of nickel [2-3], trivalent iron [4], lead [5,6], and palladium [7]. The authors of the present article have shown [8] that salicylaldoxime can be recommended not only for the quantitative determination of micro- and macro- amounts of palladium, but also for the separation of this metal from gold, platinum, ruthenium, iridium, nickel, lead, and trivalent iron.

According to published results [8-10], β-furfuraldoxime has been used (successfully) for the quantitative determination of palladium, both in pure solution and in the presence of platinum, ruthenium, iridium, nickel, copper, and trivalent iron. The present investigation was undertaken with the aim of developing a rapid and accurate method of determining large amounts of palladium in the presence of copper and nickel, with subsequent determination of the metals indicated. This problem was successfully solved by means of the two oximes—β-furfuraldoxime and salicylaldoxime.

EXPERIMENTAL

In the present investigation β-furfuraldoxime was used for determining palladium in the presence of nickel and copper contained in a solution in the ratio of Pd : Cu : Ni = 20 : 2 : 1. Subsequently, after separation of palladium, nickel and copper were determined in the filtrate by means of salicylaldoxime.

β-furfuraldoxime was synthesized by a method developed by the authors [8], which was based on a method mentioned in Syrokomsky's monograph [10].

Synthesis of β-Furfuraldoxime

Hydroxylamine hydrochloride (double the theoretical amount) is dissolved in the smallest volume of warm water (during solution of the hydrochloride considerable cooling of the water occurs—this appreciably lowers the solubility of this salt); the calculated amount of furfural is then added slowly with agitation. The beaker containing the reaction mixture is cooled with cold flowing water. After some time, oxime starts to separate out in the form of needle-like crystals. In order to speed up crystallization, the reaction mixture is stirred now and again, and is then diluted with double its volume of water. The precipitate is filtered off 6-10 hours after the onset of crystallization, and is washed thoroughly with cold water. The crude product is recrystallized from boiling 10% alcohol containing a small amount of activated charcoal. The hot solution of the oxime is filtered and left overnight to crystallize. The crystals of β-furfuraldoxime which separate out are filtered through a Buchner funnel, and are washed with a small amount of cold water and dried in a vacuum desiccator. The yield is 50-60%. The melting point of the product obtained in this way is 92°. According to published data, the melting point of β-furfuraldoxime is 91-92° [11].

1.1 g of β-furfuraldoxime dissolved in 100 ml of water at 25°, while in hot water 3.5 g dissolves.

For separating palladium from nickel and copper, the solution containing the metals indicated is diluted with water to about 100 ml, and the solution is acidified with HCl so that the final concentration of acid is 2% HCl by weight; palladium is then precipitated by continuous agitation of the solution with a 10% alcoholic solution of β-furfuraldoxime The precipitate of palladium furfuraldoximate $[Pd(C_5H_5O_2N)_2Cl_2]$, which separates out is filtered off through a No. 4 tared sintered glass crucible, and is washed with about 50 ml of 1% HCl, and finally with the same amount of water. After washing, the complex compound is dried to constant weight at 110°. The conversion factor to palladium is 0.2669.

Filtrate plus wash liquors after removal of $[Pd(C_5H_5O_2N)_2Cl_2]$ is evaporated to dryness; the organic matter is destroyed by heating with a mixture of concentrated H_2SO_4 and HNO_3. The solution is evaporated to dryness. The residue, consisting of $NiSO_4$ and $CuSO_4$ is dissolved in water (about 10-20 ml), 0.2 g of $Na(C_2H_3O_2)_2$ and 2 ml of glacial acetic acid are then added, and the copper is precipitated with a 1% aqueous-alcoholic solution of salicylaldoxime. The reagent is added in an amount sufficient to precipitate nickel and copper. The yellowish precipitate $[Cu(C_7H_6O_2N)_2]$, after coagulation by agitation, is filtered through a No. 4 tared sintered glass crucible. It is washed with a small amount of cold water (about 20 ml), and is then dried at 100° to constant weight. The conversion factor to copper is 0.1895.

Filtrate (together with wash liquors) after removal of $[Cu(C_7H_6O_2N)_2]$ is neutralized by addition of ammonia (until there is a faint odor of ammonia). The green precipitate of $[Ni(C_7H_6O_2N)_2]$ which separates out is filtered through a No. 4 tared sintered glass crucible, and is washed with cold water. The nickel salicylaldoximate is dried to constant weight at 100°. The conversion factor to nickel is 0.1774.

Palladium		Copper		Nickel	
taken	found	taken	found	taken	found
0.0312	0.0313	0.00420	0.00418	0.00192	0.00190
0.0312	0.03128	0.00420	0.00417	0.00192	0.00192
0.0312	0.0307*	0.00420	0.00413	0.00192	0.00195
0.0312	0.0310*	0.00420	0.00413	0.00192	0.00192
0.0312	0.0313	0.00420	0.00423	0.00192	0.00192
0.0312	0.0313	0.00420	0.00423	0.00192	0.00190
0.0312	0.0313*	0.00420	0.00423	0.00192	0.00192
0.0312	0.0312*	0.00420	0.00418	0.00192	0.00193
0.0624	0.0625	0.00420	0.00417	0.00192	0.00197
0.0624	0.0625	0.00420	0.00421	0.00192	0.00192
0.0624	0.0623*	0.00420	0.00424	0.00192	0.00190
0.0624	0.0622*	0.00420	0.00419	0.00192	0.00192

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* Palladium was determined by calcining to the metal.

The table contains results for determination of palladium in the presence of copper and nickel by means of α-furfuraldoxime.

SUMMARY

1. Large amounts of palladium can be successfully separated from nickel and copper (which are present in a solution together) by means of α-furfuraldoxime.

2. After the separation of palladium with α-furfuraldoxime nickel and copper can be determined in the filtrate by means of salicylaldoxime.

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AN APPARATUS FOR DETERMINING THE CONTENT OF GASES IN METALS

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The problem of determining small amounts of gases in metals has arisen in the course of the last few years in connection with the requirements of industry for pure metals. The most widely used method for determining the contents of hydrogen, oxygen, and nitrogen in metals is the method of vacuum-fusion. The method is as follows. The metal is fused in a graphite crucible (in an iron or platinum bath, or in the presence of coarse graphite powder). At high temperatures, under vacuum, dissociation of hydrides and nitrides occurs, and oxides are reduced by carbon; dissolved gases are liberated at the same time. The gases evolved are continuously pumped out of the oven and collected for analysis. Thus, the apparatus should consist of two parts – heater and analyzer. The basic requirements of the apparatus, are attainment of temperatures up to 2200°, a small value for the blank correction, and the possibility of determining small amounts of extracted gases. Various types of apparatus have been described in the literature [1-6] for determining gases in metals by the method of vacuum-fusion. Existing apparatus is not very suitable for determining the gas contents of pure metals. The apparatus of V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry for this work, however, is distinguished by the simplicity of its construction, as well as by its high efficiency. Thanks to its low blank – 0.01 ml in 15 minutes at 1800° – to the possibilities of attaining temperatures of over 2000°, and the determination of small amount of extracted gases, all metals to which the vacuum-fusion method is applicable, can be analyzed. The sensitivity of the method amounts to $1 \cdot 10^{-3}$% for oxygen and nitrogen, while for hydrogen it is $1 \cdot 10^{-4}$%.

The general appearance of the apparatus is shown in Fig. 1, while a schematic drawing is shown in Fig. 2.

In this apparatus the test metal is fused in a vacuum oven fitted with an induction heater; the gases evolved are pumped off continuously. They are then collected and analyzed.

The gases are analyzed by passing the hydrogen evolved through a palladium filter, CO is oxidized to CO_2 and the latter condensed with liquid nitrogen, while nitrogen is determined on the basis of residual pressure. An attachment to the apparatus ensures loading of the crucible without destroying the vacuum.

The major parts of the apparatus are: a vacuum oven with an induction heater, a loading mechanism, a vacuum system with DRN-50 and VN-461 pumps, a tube containing copper oxide L_{CuO}, a palladium filter P, and manometers (M_1, M_2, M_3).

A prevacuum pump VN-461 is used for evacuating the system. A mercury diffusion pump DRN-50 is used for maintaining a high vacuum throughout the system, and also for pumping out the extracted gases from the oven into the analytical flask. It should be noted that in all other current apparatus several high-vacuum pumps are used; this makes the apparatus complicated. Further, in most cases, the pumps recommended are not turned out by Russian industry and can only be made by specialist glassblowers. Traps with liquid nitrogen T-1 and T-2 are used for freezing mercury vapors.

The analytical volume is 700 ml; it is made up of connecting tubes, manometers (M_1, M_2, and M_3) and the prevacuum part of the mercury pump. The McLeod gauge M-1 measures pressures from $1 \cdot 10^{-6}$ to $2 \cdot 10^{-1}$ mm Hg, while the reversible McLeod gauge M-2 measures from $2 \cdot 10^{-3}$ mm to 3 mm Hg. Manometer M_3 is an LT-2 tube which is used for observing the process of gas evolution, their condensation in the trap, etc. In addition, a palladium filter (p) can be connected to the analytical volume, as well as a tube L_{CuO} containing cupric oxide. The palladium filter is a tube made of palladium 2.5-3.0 mm in diameter and with walls of thickness of 0.15-0.20 mm sealed off at one end. The palladium is connected to the glass via a palladium – special glass join The palladium tube is heated by means of a tungsten spiral to which current is supplied via a molybdenum join The palladium filter is heated to 600-700°. Hydrogen is pumped out through the filter by means of the mercury pump. Preliminary experiments on the separation of synthetic mixtures of H_2, CO, and N_2, showed that practically all the hydrogen diffuses through the palladium, while CO and N_2 are held back completely. It was also established that the palladium does not absorb these gases.

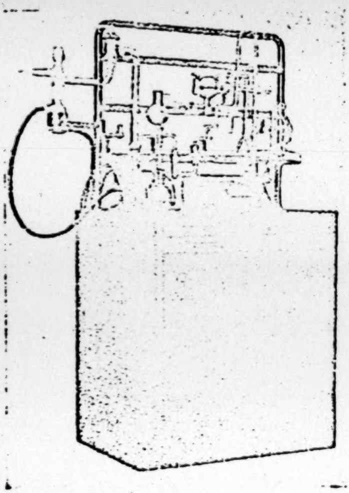

Fig. 1. General appearance of apparatus.

Carbon monoxide is oxidized to the dioxide in the tube containing cupric oxide L_{CuO}; the CO_2 is frozen in the trap with liquid nitrogen.

The loading mechanism (Fig. 3) allows one to load samples into the vacuum oven without breaking the vacuum; samples are loaded through the opening in the small pit fused into the tap of the stop cock; after rotating the tap through 120° the air is pumped out. On turning the tap through a further 120°, its opening coincides with the guiding tube of the loading mechanism and the sample falls into the crucible.

A loading mechanism of this type is very convenient for carrying out research work.

For carrying out series of analyses one can use loading mechanisms of a different type used by other authors. In such cases, samples are loaded into a tube ending in a stopper before finally assembling the vacuum oven. Samples are thrown into the crucible by means of a magnet and an iron tappet.

The first type of oven (Fig. 4) is a quartz cylinder with double walls between which water is passed for cooling. The internal diameter of the cylinder is 60 mm, the outer diameter is 85 mm, and it is 450 mm long. The cylinder is finished off at both ends in ground joints; the upper joint is used for connecting the oven to the setup, while the lower one is used for loading the crucible inside the oven. The crucible is fitted into a sectional quartz beaker with a ground lid; the latter prevents splashing of the oven walls by graphite and metal under vacuum. Fine graphite powder (100 mesh) strewn between the quartz beaker and crucible serves as a heat insulating material. The use of a heat insulating material permits one, at constant generator power, to raise the temperature to which the crucible is heated by several hundred degrees. The quartz beaker is fitted on a molybdenum wire (2 mm diameter), fused into the stopper of the lower ground joint of the oven. Crucible ($d_{ext.}$ = 22 mm, $d_{int.}$ = 15 mm; h = 38 mm) and funnel are made of graphite.

The second type of oven used is shown in Fig. 5, it is made from a quartz tube 50 mm diameter and 200 mm long, continuing into a tube 30 mm in diameter and 300 mm long. The oven is connected to the setup by means of a ground joint. Both oven and ground joint are cooled with running water. Two types of graphite crucible were used (A – $d_{ext.}$ = 18 mm; $d_{int.}$ = 12 mm; h = 97 mm, and B – $d_{ext.}$ = 14 mm; d = 8 mm h = 44 mm); these were placed in a quartz tube ($d_{ext.}$ = 27 mm; $d_{int.}$ = 24 mm; and h = 160 mm). The bottom of the tube is a ground quartz tube. Fine graphite powder (100 mesh) is strewn between the quartz tube and crucible. The quartz tube is suspended by a molybdenum wire from a brass ring which is fixed on the end of the ground joint. The use of a quartz tube instead of a graphite one used by other authors enables one to cut down the amount of gas evolved during the blank test, thereby ensuring high sensitivity for determination of gases in metals.

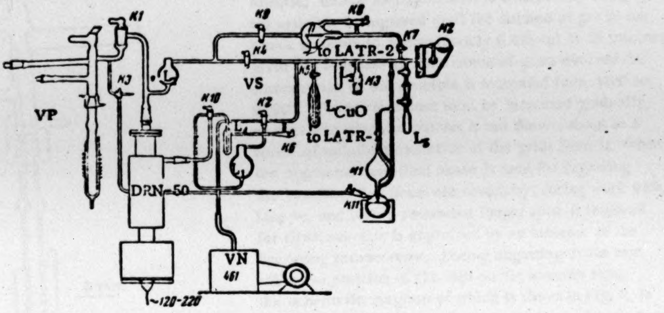
K1
K3
VP
VS
K9
K8
K4
K7
M2
to LATR-2
K5
K3
LCuO
K10
K2
L1
to LATR-1
K6
L2
M1
DRN-50
K11
VN
461
~120-220

Fig. 2. Schematic diagram of the apparatus.

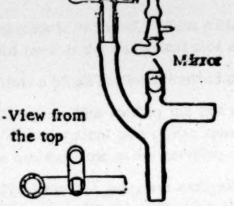
Mirror
View from the top

Fig. 3. Loading tap.

Temperature is measured by means of an optical pyrometer through a plane glass window which is protected from dust by a steel shutter operated by a magnet. An MVP-1 high frequency generator with a power of 13 kilowatts is used for heating the crucible. The high frequency circuit is mounted on a special board and can be carried along with the oven. A 100 mm circuit is used for work with the first type of oven, while for operation with the second type the circuit has a diameter of 80 mm.

Analytical Procedure

The apparatus was tried out on a whole series of metals including titanium, tungsten, molybdenum, and niobium.

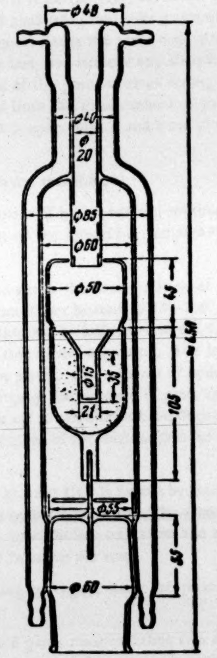
φ48
φ40
φ20
φ85
φ60
φ50
45
φ15
35
21
105
≈450
φ55
50
φ60

Fig. 4. Vacuum oven—first type.

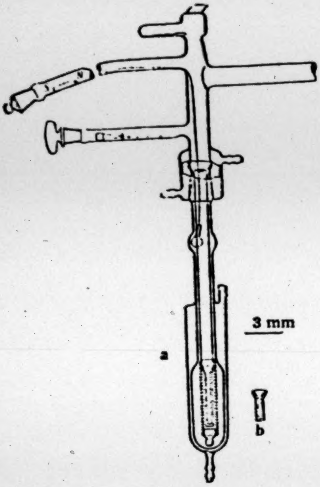

Fig. 5. Second type of vacuum oven.

The following are the basic steps in carrying out a quantitative determination of the content of gases in metals: degassing of the crucible, carrying out a blank test, loading the sample, carrying out the test with a sample. Before an experiment is carried out, the graphite crucible is degassed until the volume of gas in the blank amounts to approximately 0.025 ml in 15 minutes. With the decrease in the amount of gases evolved the temperature of the crucible is increased from 1000 to 2100°. The temperature must be increased gradually, so that fine graphite powder is not thrown about as a result of turbulent evolution of the gases from it. When the apparatus described above is used for degassing the crucible, 2-3 hours are necessary (during work with Mo, W, and Nb); a somewhat longer time is required for titanium—this is explained by an increase in the operating temperature. During degassing of the crucible the position of the taps on the vacuum setup, the schematic diagram of which is shown in Fig. 2, is as follows: tap 1 is open, taps 4 and 9 are closed, two-way tap 2 is turned towards the side of the pre-vacuum pump. On completion of degassing of the crucible, the blank test is carried out; the latter consists of collecting and analyzing the gases given off by the oven and its contents under the same conditions as are used during the test, but without any sample being present. The amount of the gases evolved during the blank is subtracted from the total amount of gas liberated when the sample is included. When a blank is being performed, tap 1 is open, taps 4 and 9 are closed, and tap 2 is turned towards the analytical side of the apparatus.

After a blank has been carried out, test sample is loaded into the crucible.

The gases liberated by the test sample are continuously pumped off by means of a mercury diffusion pump into the analytical side of the apparatus; the position of the taps on the apparatus, temperature, and extraction time are the same as for carrying out the blank.

The liberated gases are analyzed as follows: using a McLeod gauge the total pressure of the liberated gases is measured; with tap 2 closed a preliminarily degassed palladium filter heated to 600-700° is connected to the analytical volume. The positions of the taps during this operation are as follows: taps 4,5,6, and 8 are closed, taps 7 and 9 open, and tap 2 is turned towards the pre-vacuum side of the apparatus. The hydrogen diffuses through the heated palladium and is pumped off by the mercury pump. The amount of hydrogen liberated is determined from the difference in pressure before and after pumping the mixture of gases through the palladium filter. After removal of the hydrogen, a tube containing cupric oxide which has been degassed beforehand and heated to 300° is connected to the analytical volume. The positions of the various taps for this operation are as follows: taps 2,4,6,7,8 and 9 closed, tap 5 open.

CO is oxidized to CO_2 in the tube containing cupric oxide, and the CO_2 is frozen by means of liquid nitrogen $-L_3$. Any nitrogen remaining is determined on the basis of the residual pressure. The amount of oxygen can be determined both by measuring the difference in pressure of the gases before oxidation and after freezing, and by measuring the CO_2 pressure after pumping off the nitrogen and freezing the trap.

We could not use a tube containing cupric oxide for oxidizing hydrogen, since this process is a very slow one when the setup just described is used.

In working out the final results, the total amount of liberated gases must be taken into account, i.e., not only the analyzed gases but also the gases located in the pre-vacuum part of the mercury pump. Knowing the weight of test metal and the volume in which gas pressure is measured, the contents of hydrogen, oxygen, and nitrogen in the sample can be determined.

The apparatus described has been recommended by the Commission on Analytical Chemistry as a type which can be used for scientific research work and for factory laboratories occupied with determination of gases in metals.

This apparatus is in current use in factories for series analyses.

SUMMARY

An apparatus is described which can be used for the quantitative determination of the gas content of most metals. The sensitivity of the method is $1 \cdot 10^{-}$ wt. % for hydrogen and $1 \cdot 10^{-3}$ wt. % for oxygen.

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ION-EXCHANGE RESIN MEMBRANES

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Ion-exchange resins are becoming increasingly important for purification of nonelectrolytes from contamination by electrolytes, for separation of complex mixtures, for concentrating materials, and for extracting valuable ions from dilute solutions, etc. [1-5]. Ion-exchange is carried out by filtration through a layer of finely ground particles of an insoluble resin containing ionogenic groups. In order to extract an electrolyte, it is necessary to pass the solution through a column filled with grains of a cation-exchange resin which absorb the cations and, at the same time, liberate hydrogen ions into solution. The solution is then passed into a second column filled with an anion-exchange resin. In this column hydroxyl groups on the resin are replaced by anions. After a certain time – which is determined by the capacity of the ion-exchange resin and the electrolyte concentration of the solution – removal of ions by the resin ceases. Ion-exchange resins are regenerated by washing cation-exchange resins with acid, and anion-exchange resins with alkali.

Of considerable interest is simultaneous removal of cations and anions by filtration through a column packed with cation-exchange and anion-exchange resins [6,7]. Cation-exchange resins and anion-exchange resins are separated by the flotation method before regeneration. There are indications that magnetic properties can be given to cation-exchange resins. In such a case, the separation of one type of resin from the other before regeneration is carried out by means of an electromagnet [8]. A method has also been suggested for regeneration which does not involve preliminary separation of cation- from anion-exchange resin. Regeneration is carried out by successively passing solutions of alkali and ligninsulfonic acid through the column [9]. It is suggested that the grains of the anion-exchange resin are not permeable to such large molecules as those of ligninsulfonic acid; accordingly, only the cation-exchange resin is regenerated.

We think that it is more expedient to use ion-exchange resins, not as fine grains, but in the form of rods, tubes, membranes, or films for simultaneous extraction of cations and anions, since in these forms they are easier to separate before regeneration.

The discovery of a method of preparing chemically stable membranes which exhibit limiting swelling has opened up wide perspectives for using ion-exchange resins as selective diaphragms in electrolytic setups. According to available information [10-13], ion-exchange membranes, made by the Permutite Company and called Amberplex have been successfully used for extracting salts from hard water and for purifying tap water. These membranes are characterized by the following indices: limiting stability to fracture in an air-dry state – 6.6 kg/cm^2; relative elongation at fracture 40%. In a swollen state, the limiting stability to fracture is 10 kg/cm^2 and relative elongation at fracture 40%. The maximum static capacity of the cation-exchange membrane is 2.7 mg.equiv./g. Membranes can only be stored under water. The membranes break down in aromatic solvents because the binding material dissolves.

Information relating to the preparation of ion-exchange resins in the shape of any article is exceedingly scant. It has been suggested, for example, that the products of the initial stages of polycondensation of the sulfophenols or amines with formaldehyde be poured into the molds in which resinification is gradually completed [14]. Membranes can be prepared by mixing ion-exchange resin in a powdered form with thermoplastic resin – also in a powdered form (polystyrene, polymethylmethacrylate) – and pressing the mixtures in heated molds [15]. A method has been described for preparing ion-exchange resins in the form of discs or sheets, 2-3 mm thick, by pressing the ion-exchange resin on a thread of a thermoplastic resin "Saran" (a copolymer of vinylchloride and vinylidenechloride). The capacity of such discs or sheets amounts to 1mg.equiv./g, while their moisture content is 55-57% [16].

The ion-exchange membranes which we have prepared were made from a combination of powdered ion-exchange resin and binding material. The elasticity of the binding material is large enough to compensate for changes in the volume of the ion-exchange resin as a result of variations in the extent to which it swells. As a result, the membranes can be immersed in water and brought back to an air-dry state over and over again, without suffering mechanical fracture. Any ion-exchange material (any ion-exchange resin, silica gel, sulfonated coal, etc.) can be used for preparing membranes, films, or an article of any shape. The swelling capacity, porous characteristics, ion-exchange, and electrical conductivity properties of the membranes are determined by choice of ion-exchange material and the amount of it used for making the membrane. With increasing ion-exchange material content of the membrane, the stability and elasticity of the latter fall, while its capacity, swelling capacity, and electrical conductivity increase. The higher the degree of dissociation and capacity of the ion-exchange material the smaller the amount of it that is necessary to introduce into the composition of the membrane in order to get membranes of high quality.

In order to determine the stability of the membranes and films made from various ion-exchange materials with different degrees of filling, standard samples were subjected to tensile strength tests and to a number of inflexions through 180°. Tensile strength tests were carried out at 20° on a dynamometer of the Shoper type. Specific elongation at fracture was used as a measure of their elasticity.

Table 1 contains the results of tests carried out on certain types of ion-exchange membranes and films 0.5 mm thick.

Most ion-exchange resins exhibit a considerable amount of swelling in water. The use of a granulated sorbent with a high degree of swelling facilitates the process of ion-exchange, but it complicates filtration of liquids. For ion-exchange films designed for sorbents, good swelling capacity only promises an improvement in the conditions of ion-exchange. For ion-exchange membranes to be used as electrodialysis diaphragms, a lower degree of swelling coupled with the maximum possible content of ion-exchange resin is desirable. As test showed, the stability of most ion-exchange films and membranes decreases, and their elasticity increases somewhat, with increasing degree of swelling.

In Table 2 are given results for the degree of swelling of certain ion-exchange films and membranes, and the changes in their stability in the swollen state. Despite frequent changes in pH of the media, the films preserve their water permeability and their original structure.

Films and membranes behave in electrolyte solutions like the analogous ion-exchange resins prepared in granular form. By determining the acid number of various membranes and films, it was established that all the ionogenic groups of a resin are available to electrolyte ions independantly of film thickness (tests were carried out with films and membranes 0.3 to 4 mm thick). All the same, an essential drawback of these sorbents is that the rate at which ion-exchange equilibrium is established is too slow. The only exception in this connection are films made from SDV-3 (Table 3 and Fig. 1).

In Fig. 2 are given the results of tests on successive absorption of ions from a solution of calcium chloride by films of cation- and anion-exchange resins. The process was carried out under static conditions. Calcium chloride concentration in water was 1.5%. A film of the cation exchange resin SDV-3 (with the following dimensions: 25 × 25 × 1.5 mm) was immersed in the solution. Sorption was allowed to take place without stirring. After completion of ion-exchange, the film was withdrawn from the acid solution. Sorption of acid was carried out with a film of MMG or NO anion-exchange resin, whose dimensions were also 25 × 25 × 1.5 mm. The anion-exchange resin NO exhibits a larger capacity and higher basicity than the anion-exchange resin MMG; these facts are reflected in results on absorption of acid from the solution. Successive sorption of ions from more dilute solution takes place at a higher rate. In Fig. 3 are given the results of sorption of ions from Moscow tap water by means of the same ion-exchange films.

In order to check on the behavior of ion-exchange resins during simultaneous absorption of all ions from solution, a 1.5 % solution of calcium chloride in water and Moscow tap water were chosen (Fig. 4). The process was carried out under static conditions. Films of the cation-exchange resin and anion-exchange resin, both with the same dimensions of 25 × 25 × 1.5 mm, were immersed in a 250 ml beaker at a distance of 40 mm from each

TABLE 1

Stability and Elasticity of Membranes and Films in the Dry State

Designation of film	Functional groups	% resin in film	Tensile strength, kg/cm²	Specific elongation at fracture, %	Number of inflexions before fracture
KMD-P_1	—COOH	60	25,5	200	For films of type P_1
SBS-P_1	$—SO_3H$	60	31.5	206	To 250
SBS-P_2	$—SO_3H$	70	12.0	140	P_2 to 50
SBS-P_3	$—SO_3H$	90	below 2,5	1,5.	P_3 to 10
SDV-P_1	$—SO_3H$	60	5	180	
SDV-P_2	$—SO_3H$	70	below 2.5	53	
SDV-P_3	$—SO_3H$	80	below 2.5	—	
RF-P_1	$—PO(OH)_2$	60	10	190	For membranes of type M_1 to 25
SBS-M_1	$—SO_3H$	60	28	120	M_2 to 18
SBS-M_2	$—SO_3H$	70	21	65	
SBS-M_3	$—SO_3H$	80	17	40	
SDV-M_1	$—SO_3H$	60	25	110	
SDV-M_2	$—SO_3H$	70	16	60	
NO-P	Medium basic anion-exchange resin	60	30	30	M_3 to 10
MMG-P	Weak basic anion-exchange resin	60	12.5	45	
EDE-M_1	Strong basic anion-exchange resin	60	95	160—190	20
EDE-M_2	Strong basic anion-exchange resin	70	32	50—60	3—4
EDE-M_3	Strong basic anion-exchange resin	80	20	16	3—4

Notes: P_1, P_2 and P_3 – films; M_1, M_2, M_3 – membranes.

TABLE 2

Extent of Swelling of Ion-Exchange Films and Membranes and Their Stability in the Swollen State

Designation of film	% ion-exchange resin in film	Swelling in water, % by wt.	Decrease in tensile strength, as % of the original	Increase in specific elongation at fracture as % of the original
KMP-P_1	60	350	50	0
SBS-P_1	60	25	12.8	17.8
SBS-P_2	70	29	45.1	—
SBS-P_3	80	36	46.0	150
SDV-P_3	70	120	50	250
EDE-P_1	60	46	10	25
EDE-P_2	70	64	14	8
NO-P_1	60	2.5	0	0
MMG-P_1	60	20	25	40
SBS-M_1	60	18	14	15
SBS-M_2	70	20	27	12
SBS-M_3	80	28	47	12—14
SDV-M_1	60	85	50	300
SDV-M_2	70	96	75	300—320
EDE-M_1	60	20	45	24
EDE-M_2	70	28	55	28

Note: Swelling of films and membranes was determined by keeping them in water for 72 hours. The thickness of the films in the dry state was 0.45-0.62 mm.

TABLE 3

Characteristics of the Ion-Exchange Properties of Films

Designation of film	Ionogenic group	Swelling in water, in %	Thickness of films in swollen state, mm	Volume of films in the swollen state cm^2	Acid No. in mg-equiv./g	Total capacity (calcium ions) in mg.equiv./g	Rate at which 50% capacity is reached (Na ions) in min.
KMD-P_1	—COOH	350	0.6	0.36	4.05	—	1620
RF-P_1	—$PO(OH)_2$	65	0.05	0.45	3.6	2.02	60
SDV-P_1	—SO_3H	90—100	0.03	0.52	2.4	2.2	6
SBS-P_1	—SO_3H	25	0.58	0.7	1.81	1.8	1320
SBS-M_1	—SO_3H	18	0.32	0,98	1.83	1.8	1240
SDV-M_1	—SO_3H	85	0.45	0,59	2.2	2.2	5

Notes: Determinations of acid number, static capacity with respect to calcium ions, and rate of establishment of ion-exchange equilibrium were carried out by methods which are used for granular ion-exchange sorbents.

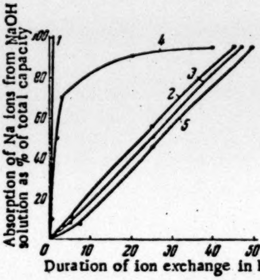

Fig. 1. Rate at which ion-exchange equilibrium is established for ion-exchange membranes from 0.5 N NaOH in the case of KMD, and 0.5 N $CaCl_2$ for the rest of the types: 1) film SDV-3; 2) film SBS; 3) membrane of SBS; 4) film of RF; 5) film of KMD.

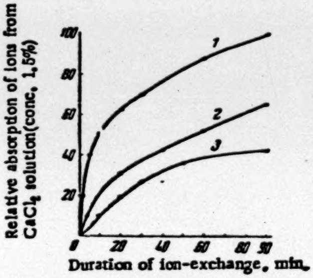

Fig. 2. Kinetics of the process of ion-exchange between films and ions for solutions of calcium chloride, during successive sorption under static conditions: 1) membrane of SDV-3; 2) membrane of NO; 3) membrane of MMG.

other. Solution temperature was 20°, sorption was allowed to proceed without agitation. The results show that a one-state ion-exchange process improves reaction conditions for each ion-exchange resin. Thus, when films of SDV-3 and NO are used together complete removal of all ions from water was achieved in 25-30 minutes. By agitating the solution or raising the temperature, it is possible to achieve an even greater rate for the ion-exchange process.

The possibility of using the films and membranes we have suggested is being studied by the All Union Scientific Research Institute for Water Supply, Sewer Systems, Hydraulic Structures, and Hydrogeological Engineering (VODGEO) (see e.g., [13, 17]). According to the result of these studies, the specific volume electrical resistance of membranes containing 65% of ion-exchange resin is 70-250 ohm.cm, depending on the choice of resin, while the transport number of ions of the same charge is 0.94.

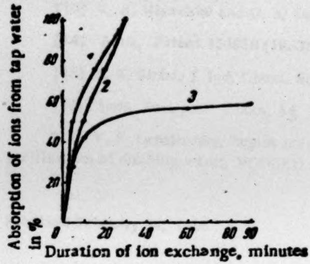

Fig. 3. Kinetics of the process of ion-exchange between films and ions in Moscow tap water during successive sorption under static conditions: 1) membrane of SDV-3; 2) membrane of NO; 3) membrane of MMG.

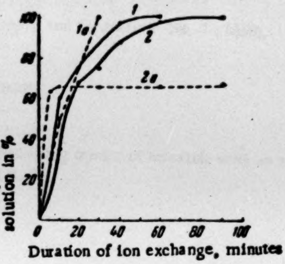

Fig. 4. Kinetics of the ion-exchange process between films and ions when the following combination of films were used: SDV-3 + MMG or SDV-3 + NO. 1) membranes of SDV-3 and NO; 1a) membranes of SDV-3 and NO; 2) membranes of SDV-3 and MMG; 2a) membranes of SDV-3 and MMG. – from 1.5% $CaCl_2$ solution; --- from tap water.

SUMMARY

1. The use of high-swelling ion-exchange films or membranes for simultaneous removal of cations and anions from solution facilitates subsequent regeneration of the ion-exchange resins and facilitates purification of viscous solutions.

2. A method has been devised for preparing ion-exchange membranes and films which enables one to change – within very wide limits – their size, elasticity, swelling capacity, water-permeability, capacity, and electrical permeability. Any ion-exchange sorbents can be used for the production of these films and membranes.

3. The ion-exchange properties of the films and membranes are similar to those of the corresponding granulated ion-exchange resins.

4. The use of ion-exchange films in sorption and electrodialysis processes means that use can be made of dust waste from the industrial production of ion-exchange sorbents.

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SENSITIVITY OF DETECTION OF MAGNESIUM IONS BY MEANS OF IODINE

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Gay-Lussac [1] was the first to observe formation of a reddish-brown compound during the action of iodine on magnesium oxide in the presence of water. Schlagdehauffen [2] used a 2% solution of iodine in sodium hydroxide as a reagent for detecting magnesium in solution. Deniges [3] showed that it was possible to use the reaction just mentioned for the qualitative detection and semi-quantitative determination of magnesium in sea water by means of a spot technique. Van Eck [4] suggested carrying out a qualitative test for magnesium ions on filter paper discs soaked in an iodine solution and in dilute alkali. V. I. Petrashen and V. I. Kuznetsov [5, 6] established the limiting concentrations and also studied the chemistry of the reaction. In more recent papers [7-12], results have been given for the sensitivity of the reaction for magnesium ions in pure solutions, and various procedures have been outlined for carrying out the reaction—these include detection of magnesium in the presence of interfering ions.

All the same, although this color reaction for magnesium ions in which use is made of iodine has been known for a long time and is widely used at present it has not been studied sufficiently. There is no published information about limiting ratios; results for limit of identification and limiting concentration are contradictory. Thus, V. I. Petrashen, in one of his papers [5], indicates that in a solution of pure magnesium salt at a dilution of 1: 41,200 there is observed formation of a reddish brown precipitate as soon as the reagent is added; at a dilution of 1: 123,000 a precipitate forms after 2 minutes, while at a dilution of 1: 246,000 appearance of a precipitate is difficult to observe. The same author, in a later article [13], gives a value for the limiting concentration of magnesium for the same reaction of 1: 82,400.

According to Faigl [14], the limiting concentration is found at a ratio of 1: 165,000 and finally, in the second report of the International Commission on New Analytical Reactions and Reagents [15], the limiting concentration is said to be 1: 15,000.

We have determined the limiting concentration and limiting ratios for ions of the alkaline-earth metals, K^+ and Na^+ and NH^+, not only for reaction with iodine, but also, for comparison, with magneson and quinalizarin. In order to get comparative results for the effect of the alkali and alkaline-earth metals on the sensitivity of the reactions mentioned above, the limiting ratios were fixed for one and the same concentration of magnesium in solution – 6 γ/ml.

Approximately 1 N solution of iodine was prepared by dissolving the appropriate amount of sublimed iodine in an aqueous potassium iodide solution containing the minimum amount of potassium iodide to dissolve the iodine [16]. The solution of magneson used was a 0.1% solution of analytical grade reagent in 50% ethanol, while the quinalizarin solution was a 0.01% solution of analytical grade reagent in ethanol. An approximately 2 N solution of sodium hydroxide, free from carbonate, and prepared by diluting a saturated solution filtered beforehand through a No. 4 sintered glass crucible, was used in all experiments. Test solutions of magnesium were prepared by diluting a standard solution of magnesium chloride whose concentration had been established gravimetrically by the 8-hydroxyquinoline method [17].

Experiments to establish limiting ratios and limiting dilutions were carried out in test tubes containing 1 ml of the magnesium solution. Blank tests were carried out in parallel in each case with 1 ml distilled water.

For determining limiting ratios, the order of addition of reagents was the same in each case: to 1 ml of solution containing magnesium and one of the alkali or alkaline-earth metals ions was added 2 drops of reagent, the contents were then shaken and 2-3 drops of alkali added. Formation of a precipitate or change in color of the solution was observed against a white background.

Changing the order of addition of the reagent at magnesium concentrations of 6γ/ml, both for pure solutions of magnesium and for solutions containing magnesium as well as ions of the alkali or alkaline earth metals does not affect the sensitivity of the reactions studied. For reactions in pure solutions of magnesium, when magneson and quinalizarin are used as reagents, changes in the order of addition of reagents did not lead to changes in sensitivity at magnesium concentrations near to limiting dilution. When iodine is used as reagent at magnesium concentrations less than 6γ/ml, as preliminary experiments showed, changes in the order of addition of reagents, as well as changes in the method of observing the reaction effects, may lead to an increase in the sensitivity of ten or even a hundred times; this is not observed under the same conditions when magneson and quinalizarin are used. Experiments results are given in the Table.

TABLE

Limiting Ratios for Magnesium Detection

Reagent	Limit of identification and dilution for pure solutions of magnesium salts		Limiting ratios for 6γ Mg/ml					
	limit of identification	limiting dilution	Mg : Ca	Mg : Sr	Mg : Ba	Mg : Na	Mg : K	Mg : NH_4
I_2 + NaOH	0.2	$\frac{1}{5000000}$	$\frac{1}{8000}$	$\frac{1}{7000}$	$\frac{1}{4500}$	$\frac{1}{18700}$	$\frac{1}{21600}$	$\frac{1}{1500}$
Magneson	2	$\frac{1}{500000}$	$\frac{1}{200}$	$\frac{1}{6000}$	$\frac{1}{32100}$	$\frac{1}{18700}$	$\frac{1}{21600}$	$\frac{1}{500}$
Quinalizarin	4	$\frac{1}{250000}$	$\frac{1}{400}$	$\frac{1}{12000}$	$\frac{1}{32100}$	$\frac{1}{18700}$	$\frac{1}{21600}$	$\frac{1}{550}$

We succeeded in detecting magnesium reliably in solution by means of iodine at a concentration of 0.2γMg/ml by using the following technique.

To 1 ml of a solution of a magnesium salt was added 2-3 drops of alkali; the contents of the tube were shaken for 2-3 minutes and then iodine solution added until a well defined yellowish brown color is obtained. Under these conditions, formation of a red-brown precipitate cannot be observed at concentrations of 0.2-0.4 γMg/ml; the negligible amount of precipitate that is nevertheless formed is found in the form of a fine suspension in the solution, for the most part on the surface of the liquid. By careful shaking of the test tube contents it is easy to collect the precipitate on the inner walls of the test tube, at a distance of 1-1.5 cm from the liquid surface in the form of a red-brown ring which is clearly defined against a white background. By means of this technique it is possible, using iodine for detecting magnesium, to find traces of magnesium in ordinary distilled water which has been kept for a long time in glass vessels.

According to published data, when organic reagents (magneson, quinalizarin) and iodine are used for detecting magnesium, ammonium salts interfere or depress the sensitivity of the reaction considerably because they dissolve magnesium hydroxide. There are no indications of the limiting ratio at which it is still possible, with confidence, to detect magnesium in the presence of ammonium ions.

We determined limiting ratios at 6γMg/ml, not only for the alkaline-earths, Na^+ and K^+, but also for ammonium ions (see Table). We found that an appreciable amount of ammonium compounds (1:500, 1:600) does not interfere with the formation of colored precipitates when magneson and quinalizarin are used.

When iodine is used as a reagent for magnesium, even negligible amounts of ammonium salts in alkaline solution lead to the formation of black nitrogen iodide, which prevents observation of the formation of the red-brown precipitate with magnesium.

In order to eliminate interference from nitrogen iodide we used hydrogen peroxide to decompose it in alkaline media. From published data [18,19], it is known that nitrogen iodide in the presence of water and alkali decomposes according to two processes which occur simultaneously:

$$\text{I.}\ NI_3 \cdot NH_3 \rightarrow N_2 + 3HI;$$

$$\text{II.}\ NI_3 \cdot NH_3 + 3H_2O \rightarrow 2NH_3 + 3HIO.$$

When excess iodine solution is added to a solution of an ammonium salt in the presence of NaOH, and a few drops of 3% hydrogen peroxide then added, the black precipitate of nitrogen iodide which is formed decomposes immediately to give colorless gaseous products, while the solution becomes perfectly colorless. Even traces of ammonia could not be detected in a solution treated in this way, when the most sensitive tests were applied. It is possible that hydrogen peroxide catalytically accelerates reaction (I) and the solution is completely freed from ammonium salts.

Iodine was used as a reagent for the qualitative detection of magnesium in the presence of ammonium salts as follows: to 1 ml of test solution containing magnesium and ammonium salts was added 2-3 drops of alkali followed by 4-6 drops of iodine solution. Depending on the amount of ammonium salts in solution, the solution acquired a black color, or black nitrogen iodide precipitated out. 1-2 drops of 3% hydrogen peroxide were then added and the test tube and its contents shaken. The nitrogen iodide decomposed turbulently as soon as mixing commenced to give off nitrogen and oxygen, and in most cases the solution became completely colorless. When the solution did not become completely colorless, another drop of hydrogen peroxide was added. When large amounts of ammonium salts were present in solution, alkali, iodine, and peroxide were again added in the same order as before, until the black precipitate of nitrogen iodide ceased to be formed on addition of alkali and iodine.

To a solution treated in this way was then added iodine solution dropwise until a pronounced yellow-brown color was observed; formation of the red-brown precipitate of the adsorption compound of magnesium hydroxide with iodine was then followed by observation against a white background. At low magnesium concentrations (near to the limiting dilution) formation of a colored precipitate in the solution could not be observed. In such cases formation of a red-brown ring on the inner walls of the test tube was observed, as described before for the case of solutions of pure magnesium salts. Using this technique, it is possible to detect magnesium with confidence in the presence of ammonium salts by means of iodine at ratios of $Mg^{2+} : NH_4^+ = 1:1500$.

The results given in the table show that an iodine solution is a more sensitive reagent for magnesium ions than the organic reagents examined. One can detect magnesium reliably in the presence of large amounts of alkaline-earths, as well as Na^+, K^+, and NH_4^+. Magneson and quinalizarin are less sensitive reagents and have lower limiting ratios for calcium. The extent of the influence of Ca, Sr, and Ba in the series Ca – Sr – Ba on detection of magnesium by means of an iodine solution, and by the two organic reagents considered, varies.

When iodine is used as reagent in the series Ca – Sr – Ba, with increasing solubility of the metal hydroxides the limiting ratios decrease, while for magneson and quinalizarin the corresponding limiting ratios increase.

Na^+ and K^+ do not have an appreciable effect on the sensitivy of the reaction for magnesium ions for all the listed reagents. The limiting ratios found for sodium of 1:18700 and for potassium of 1:21600 correspond to concentrations of sodium and potassium in the test solution approaching saturation for the chlorides of these elements at a concentration of Mg of 6γ Mg/ml.

SUMMARY

1. The effect of Ca^{2+}, Sr^{2+}, Ba^{2+}, K^+, Na^+ and NH_4^+ ions on the sensitivity of detection of magnesium ions by means of iodine, magneson, and quinalizarin has been studied; the respective limiting ratios at 6γ Mg/ml have been found.

2. When magnesium is detected by means of iodine the limiting ratios in the series Ca – Sr – Ba decrease as the solubility of the respective hydroxides increases; these ratios increase, however, when magneson and quinalizarin are used.

3. A method has been developed for detection of magnesium by means of iodine. The method permits reaction sensitivity to be increased to 0.2 γ Mg/ml, and allows magnesium to be detected in the presence of large amounts of ammonium salts.

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A POTENTIOMETRIC METHOD OF DETERMINING SMALL AMOUNTS OF BARIUM IN NICKEL BASED ALLOYS BY MEANS OF COMPLEXONE III

L. Ya. Polyak

Development of a method for the complexonometric determination of small amounts of barium (0.05-0.5%) in nickel based alloys containing significant amounts of chromium, tungsten, molybdenum, titanium, niobium, iron, aluminum, as well as other metals present as impurities, is of undoubted practical interest.

A method has been published [1] for volumetric titration of barium salt solutions with disodium ethylenediaminetetracetate. In order to get a better defined color transition at the titration end point, it is recommended that some magnesium chloride and calcium chloride be added to the solution being titrated before its standardization. The indicator used is a dry mixture of Eriochrome Black T and sodium chloride. The gravimetric method of determining barium as the sulfate has been improved by dissolving the barium sulfate in an ammoniacal solution of Complexone III, with subsequent acidification of the solution; pure $BaSO_4$ is thereupon precipitated [2]. Of other methods, mention may be made of precipitation of barium with organic reagents: sulfamic acid [3], ethyl sulfate, methyl sulfate [4, 5], which hydrolyze slowly with liberation of sulfate ions at 96-97°. The coarse crystalline precipitate of barium sulfate formed under these conditions can be easily filtered, and only contains small amounts of adsorbed materials. Potentiometric [6] and amperometric [7] methods of titrating barium with potassium dichromate are only applicable to the determination of large amounts of barium.

At pH 10-12, the alkaline-earths react stoichiometrically with Complexone III. Volumetric complexometric titration of barium with Eriochrome T, in view of the instability of the compound of barium with the indicator, is only applicable when a calcium or magnesium salt is added to the solution of Complexone III before its standardization [1]. We thought it best to develop a potentiometric method for determing small amounts of barium. Přibil has described a potentiometric method of titrating a number of cations with Complexone III in weakly acid buffered solution [8, 9]. Since titration of cations in weakly acid solutions in the pH range [1-6] is based on oxidation-reduction processes, Pribil used a platinum electrode as the indicator electrode for titrating such solutions. Since barium only gives stable compounds with Complexone III in ammoniacal media at pH 11-12, in order to establish the possibility of carrying out potentiometric titration of barium in ammoniacal media we tested a number of metals as potential electrodes. We found that barium and other cations can be titrated in ammoniacal media (pH 11-12) with Complexone III, by using a tungsten electrode as the indicator electrode; a molybdenum electrode can also be used, but it is not so suitable as the tungsten electrode. Other metals (antimony, chromium, nichrome, aluminum, and platinum) proved unsuitable.

During direct and back titration of barium in ammoniacal media with Complexone III, using the pair of metals Pt – W, tungsten acts as the indicator, while platinum acts as the reference electrode. In order to establish how each of these electrodes behave during titration, experiments were carried out in which 0.01 N solutions of barium chloride were titrated with Complexone III, and Complexone III was titrated with barium chloride; in these experiments the following pairs of electrodes were tried: Pt – W, W – calomel electrode; and Pt – calomel electrode. Potential difference was determined by a compensation method.

The titration curves (Figs. 1, 2, and 3) show that during titration of Complexone III with barium chloride the potential of the platinum electrode remains unchanged, while the potential of the tungsten electrode changes sharply at the equivalence point. Titration curves obtained with the pair Pt – W are similar to titration curves obtained with W – calomel electrode. The electrochemical behavior of electrodes during potentiometric titration of barium in ammoniacal media with Complexone III has been described in detail previously [11].*

In order to establish the possibility of carrying out a potentiometric titration of small amounts of barium with Complexone III, the following experiments were carried out: to various amounts of a standard solution of barium chloride (from 0.1 to 0.5%) was added 10 ml of an ammoniacal buffer mixture (8.5 g NH_4Cl + 115 ml NH_4OH dissolved in 1 liter H_2O) and 20 ml of 0.01 N Complexone III solution, and excess Complexone III back titrated with 0.01 N barium chloride potentiometrically, using the electrode pair Pt – W. The ratio of the concentrations of 0.01 N Complexone III solution and barium chloride solution was established under the same conditions. Titration results are adduced in Table 1.

TABLE 1

Indirect Potentiometric Determination of Small Amounts of Barium in Solutions of Pure Barium Salts

Ba taken, in %	Ba found, in %	Ba taken, in %	Ba found, in %
0.11	0.11: 0.11	0.44	0.43: 0.43
0.22	0.23: 0.23	0.16	0.16: 0.16
0.33	0.34: 0.33	0.27	0.27: 0.27

On attempting to determine even smaller amounts of barium (from 0.01 to 0.1%) by means of 0.001 N solutions of Complexone III and barium chloride, we could not get satisfactory results.

Direct potentiometric titration of more than 0.05% barium with Complexone III also gave completely satisfactory results (Table 2). In order to develop a potentiometric method of determining small amounts of barium in heat resistant alloys based on nickel, we used the property of barium sulfate of dissolving in an ammoniacal solution of Complexone III [2]. After quantitative extraction of barium from the alloys as the sulfate, it was dissolved in a known excess of dilute (0.01 N) Complexone III solution; the latter was then back titrated potentiometrically with barium chloride solution.

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* The bimetallic electrode pair Pt – W has also been used by L. M. Budanova and O. P. Platonova [11], for determining a number of cations by means of Complexone III. Their article needs looking at, since it contains false conclusions. The authors state that in their work they succeeded in carrying out direct titration of metals which do not exhibit variable valency (Zr, Cd) with Complexone III; this seems to contradict Pribil's experiment – the latter was the first to use Complexone III for potentiometric titration [8, 9]. Budanova and Platonova wrong. Pribil titrated cations in a weak acid buffered solution (pH 3-6) using a platinum electrode as the indicator electrode. Because the cations possess variable valency, they form complexes of varying stability, an oxidation-reduction system is formed in solution, and the potential change of the indicator platinum electrode during titration is similar to that observed during normal redox titrations.

In cases where the metal cation does not exhibit variable valency, Pribil suggests back titration of excess Complexone III with ferric chloride; i.e., he proposes the creation of an oxidation-reduction system by titrating with a solution of the salt of a metal whose ions exhibit two valency stages (Fe^{2+} and Fe^{3+}) and which give complexes of different stability with Complexone III. Thus, Pribil treated the question of direct and back titration with Complexone III as an oxidation-reduction system, the platinum being used as an indicator electrode.

L. M. Budanova and O. P. Platonova used the electrode pair Pt – W for direct and back titration of elements in ammoniacal media with Complexone III, and mistakenly assumed that in their case the platinum was the indicator electrode.

In due course it has been established that the pair of metals Pt – W can be used in a whole series of oxidation-reduction reactions [12], and can replace the pair Pt – calomel half element. Budanova and Platonova mistakenly identified the use of this pair for titration of oxidation-reduction systems with titration of simple systems in ammoniacal media Complexone III. In the first instance, the platinum electrode (which is a transmitter of electrons serves)as the indicator electrode during titration; the tungsten electrode acts as reference electrode. In the case of titration of cations in ammoniacal media with Complexone III, using the pair of electrodes Pt – W, the character of the electrode processes, as we have shown in detail before [10], is completely different; tungsten is now the indicator electrode and platinum the reference electrode.

TABLE 2

Direct Potentiometric Titration of Barium with Complexone III

Ba taken in %	Ba found in %
0.11	0.11: 0.11
0.165	0.164: 0.165
0.22	0.22: 0.22
0.27	0.264: 0.200
0.33	0.32: 0.32

TABLE 3

Determination of Barium after its Separation as $BaSO_4$

Ba taken in %	Ba found in %
0.11	0.10: 0.11
0.17	0.17: 0.18
0.22	0.20: 0.20
0.33	0.33: 0.33
0.23	0.23: 0.24
0.28	0.28: 0.28

In order to check on the completeness of solution of barium sulfate in the dilute Complexone III solution, the barium was precipitated as sulfate from various amounts of a standard solution of barium chloride (from 0.1 to 0.5%). The precipitate was filtered through an ashless filter, transferred to a porcelain crucible and ignited at 700-800°. The dry residue was transferred to a beaker and dissolved in a known amount of an ammoniacal solution of Complexone III taken in excess; 10 ml of ammoniacal buffer solution was added and excess Complexone III back titrated potentiometrically with 0.01 N barium chloride.

The results obtained are given in Table 3.

Baroi, cam be determined by this method with an accuracy of 0.01%.

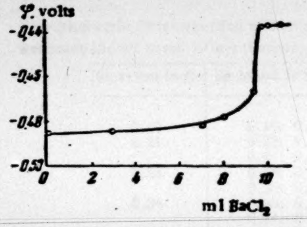

Fig. 1. Potentiometric titration curves of Complexone III with $BaCl_2$ solution using the electrode pair W – Pt.

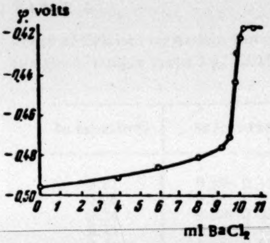

Fig. 2. Potentiometric titration curve of Complexone III with $BaCl_2$ solution using the electrode pair W – calomel half element.

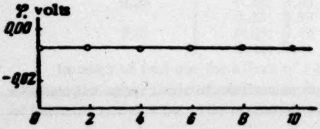

Fig. 3. Potentiometric titration curve of Complexone III with $BaCl_2$ solution using the electrode pair Pt – calomel half element.

Determination of Barium in Heat Resistant Alloys Based on Nickel

In order to determine barium in alloys on nickel, it is first of all necessary to establish the optimum conditions for the quantitative separation of barium as the sulfate from the alloys, and, secondly, to improve purification of the barium sulfate.

Barium sulfate was purified by treating the precipitate on the filter with 0.1 N Complexone III solution. During this process impurities such as nickel, chromium, aluminum, manganese, and iron which form soluble, stable, complex compounds with Complexon III at pH 5-6, pass into the filtrate; at this pH the barium sulfate precipitate does not react with Complexone III. By subsequent solution of the barium sulfate in an ammoniacal solution of Complexone III, the barium is completely freed from contamination by silicic and niobic acids. Thus only pure barium sulfate is finally in solution in the ammoniacal solution of Complexone III.

Barium can be determined in nickel based alloys as follows: 1 g of alloy is dissolved on heating in distilled hydrochloric acid.* When solution is complete, the solution is evaporated to a volume of 20 ml. Without filtering off the carbides which separate out, the solution is diluted to 250-300 ml and allowed to stand in a warm place for 1-1/2 to 2 hours. When this is done, the readily decomposable carbides dissolve, while a considerable amount of such elements as tungsten, niobium, and possibly titanium, is precipitated as the result of hydrolysis. The hot solution is filtered and the filter washed 3-4 times with water. To the filtrate is added another 10 ml of hydrochloric acid and the solution diluted to 300 ml; the solution is then heated to boiling and barium precipitated by adding 5 ml of sulfuric acid (diluted in the proportion of 1 : 5). Precipitation is affected by friction of a glass rod on the beaker walls.

The next day the precipitate is filtered through 3 filters (blue ribbon quality) and treated on the filter with 0.1 N Complexone III solution. Filter and precipitate are ignited in a porcelain crucible at 700°. The dry residue is transferred to the beaker in which precipitation was carried out, and is dissolved in 20 ml 0.01 N ammoniacal Complexone III solution. Solution takes time; accordingly, the precipitate of $BaSO_4$ is left in the ammoniacal solution of Complexone III for some time. Excess unreacted complexone is potentiometrically titrated with 0.01 N barium chloride, using the electrode pair Pt — W. When the barium sulfate has dissolved there remains a fair amount of insoluble residue, mainly silica, but also containing some iron and niobium. Potentiometric titration of excess unreacted Complexone III is carried out in presence of this precipitate without filtering it off.

Results for barium determination are given in Table 4.

TABLE 4

Potentiometric Determination of Barium in Heat Resistant Nickel Based Alloys (Sample weight 1 g)

Ba taken in %	Ba found in %
0.14	0.14: 0.15
0.21	0.22: 0.20
	0.21: 0.21
0.28	0.28: 0.28
	0.30: 0.28
0.34	0.34: 0.34
	0.34: 0.34
0.40	0.39: 0.39
	0.37: 0.40
0.17	0.176: 0.19
	0.176: 0.18
0.23	0.22: 0.23
	0.22: 0.24
0.35	0.35: 0.35
	0.33: 0.36
0.41	0.39: 0.40
	0.41: 0.41

TABLE 5

Effect of Calcium on Barium Determination (weight of sample taken 1 g, 0.03% Ca added)

Ba taken in %	Ba found in %
0.17	0.19: 0.19
0.25	0.26: 0.26
0.34	0.34: 0.35
0.45	0.44: 0.42
0.24	0.25: 0.25
0.27	0.26: 0,28
0.29	0.29. 0.29
0.32	0.30: 0.31
0.35	0.35: 0.35
0.20	0.21: 0.21
0.23	0.24: 0.25
0.25	0.27: 0.27
0.30	0.31: 0.31

In order to find out the effect of calcium in test samples of heat resistant alloys, a constant amount of calcium (the upper limit of calcium in the alloys) was also added to the samples, in addition to varying amounts of barium (0.15-0.4%). The results obtained in this case are given in Table 5.

Calcium was found to have no effect at all on the potentiometric determination of barium. Table 6 shows the unsuitability of a gravimetric method, without preliminary purification of the precipitate, for determination of small amounts of barium in alloys of a complex nature.

Completely satisfactory results were also obtained (Table 7) during potentiometric determination of

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* In order to check on the reliability of the method we first took alloys completely free of barium, and added a known amount of standard solution of barium chloride before dissolving the alloys.

TABLE 6

Gravimetric Determination of Barium in Heat Resistant Alloys

Ba added in %	Ba found in %	Ba added in %	Ba found in %
0.11	0.14 0.22	0.06	0.30 0.25
0.17	0.15 0.20	0.11	0.31 0.30
0.23	0.12 0.56	0.17	0.30 0.25 0.27
0.28	0.21 0.40		
0.34	0.47 0.40	0.28	0.44 0.27
Blank	0.25	0.34	0.41 0.39
		Blank	0.22

TABLE 7

Determination of 0.05-0.1% Ba in Alloys

Ba added in %	Ba found in %	
	total	in the alloy
0.17	0.28; 0.28	0.11; 0.11
0.28	0.39; 0.39	0.11; 0.11
0.25	0.34; 0.34	0.09; 0.09
0.12	0.18; 0.18	0.06; 0.06
0.17	0.21; 0.22	0.04; 0.05
0.15	0.31: 0.31	0.06; 0.06
0.25	0.33; 0.34	0.08; 0.09
0.31	0.40; 0.40	0.09; 0.09
0.25	0.30; 0.31	0.05: 0.06
0.31	0.36; 0.36	0.05; 0.05

hundredths of a percent of barium in nickel alloys by the method of additions.

SUMMARY

1. The possibility has been demonstrated of carrying out a potentiometric determination of small amounts of barium (from 0.05 to 0.5%) in solutions of pure barium chloride salts by means of 0.01 N Complexone III solution.

2. A new method has been developed for the potentiometric determination of small amounts of barium in heat resistant alloys based on nickel. Barium is isolated as the sulfate and the sulfate is then dissolved in an ammoniacal solution of Complexone III; excess of the latter is back titrated potentiometrically with a solution of barium chloride using the electrode pair Pt – W.

3. By means of this method it is possible to determine more than 0.05% of barium in the presence of calcium in multicomponent alloys. The method of additions should be used for alloys containing 0.05-0.20% of Ba.

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RAPID METHODS OF DETERMINING SMALL AMOUNTS OF SELENIUM

PART I. A PERMANGANOMETRIC METHOD

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Under the effect of strong oxidizing agents, elemental selenium is oxidized to form compounds which are soluble in water and have a valency of +4 or +6.

At the same time compounds of selenium are readily reduced to the elemental state. These properties of selenium have enabled a method to be developed for its determination which is based on precipitating it in the elemental form from test solution by the action of a suitable reducing agent. The selenium which is then separated from the solution by filtration or centrifuging is brought into solution by the action of a strong oxidizing agent, and is determined in solution either by back titration of excess oxidizing agent, or on the basis of the color of the solution obtained after reduction of selenium to the elemental state in the presence of a stabilizer, or on the basis of the reactions of the selenate or selenite ions with organic reagents after destruction of excess oxidizing agent.

As a result of tests with a large number of oxidizing agents potassium permanganate, potassium dichromate, and quadrivalent cerium sulfate were chosen. Reducing agents which have been used include sodium sulfite, sulfurous acid, and Mohr's salt.

Gooch and Clemons [1] were the first to use permanganate for titrimetric determination of selenium. Gaev [2] used potassium permanganate for determining selenium in matte. To the filtrate from the residue insoluble in acids and containing selenious acid is added potassium permanganate, excess of which is titrated with oxalic acid. Under these conditions high results are obtained since tellurium is also titrated by permanganate. In order to get accurate results, tellurium must be determined on a separate aliquot. Titova [3] developed a permanganometric method for determining selenium in solutions of selenious acid obtained by dissolving selenium in nitric acid; she titrated selenious acid with a solution of potassium permanganate in sulfuric acid. By her method it is possible to determine 0.2-0.02 mg of selenium in 1.0-0.1 ml of test solution.

EXPERIMENTAL

We used potassium permanganate for titrating selenium since it shows a number of advantages over other oxidizing agents (a fairly high oxidation-reduction potential, the absence of the need of using an indicator). Potassium permanganate [4] reacts with elemental selenium in acid solution according to the equation:

$$6KMnO_4 + 5Se + 9H_2SO_4 \rightarrow 3K_2SO_4 + 6MnSO_4 + 5H_2SeO_4 + 4H_2O.$$

The reaction is fairly rapid, particularly when heat* is applied and excess permanganate used. Under these conditions, selenium is oxidized to the sexivalent state. The fact that this oxidation-reduction process goes so far is explained by the significant difference in the potentials of the systems MnO_4^-/Mn^{2+}, SeO_3^{2-}/Se and SeO_4^{2-}/SeO_3^{2-} which are respectively +1.52, +0.74, and +1.09 volts.

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* $KMnO_4$ decomposes on heating strongly.

till a greenish solution was formed.* 1 ml of 0.02 N potassium permanganate was added (from a microburet) to the solution and the mixture shaken, while warming gently, till the selenium had dissolved completely. Exactly 1 ml of 0.02 N solution of Mohr's salt was then added and the mixture shaken until the red color had disappeared completely. 1-2 g of sodium pyrophosphate was added and dissolved. The solution obtained was titrated with 0.02 N potassium permanganate from the same microburet until a stable rose color was obtained which did not disappear in the course of 1-2 minutes.

The total amount of permanganate solution used during the titration before and after addition of the solution of Mohr's salt was noted.

The amount of selenium was calculated by means of the formula

$$A = (K_1V_1 - K_2V_2) \cdot 0.01316,$$

where A is the amount of selenium in the sample in mg ; K_1 — normality of the permanganate solution; V_1 — the volume of permanganate used; k_2 — normality of the Mohr's salt solution; V_2 — volume of the Mohr's salt solution. Results of these determinations are given in Table 1.

TABLE 1

Micro-determination of Selenium by Permanganometric Titration of Pure Solutions

Amount of Se in the test, in mg		Difference in mg
found	taken	
0.7850	0.7892	—0.0042
0.7860	0.7892	—0.0032
0.1550	0.1580	—0.0050
0.1570	0.1580	—0.0010
0.0160	0.0 58	+0.0002
0.0150	0.0 58	—0.003
0.0083	0.0079	+0.0004
0.0070	0.0079	—0.0009

Differences in the individual determinations of selenium lie within the limits of 0.001 to 0.004 mg (Table 1). In most cases the values actually found are lower than the theoretical values. The reasons for the low results have not been established hitherto. Bearing in mind the low selenium contents of the samples, the results can be regarded as satisfactory.

b) Determination of Selenium in the Presence of Other Elements

Elements which exhibit variable valency, as well as oxidizing ions (Fe^{II}, Cu^{2+}, Cr^{VI}, As^{V}, Sb^{V}, Sn^{IV}, NO_2^-, Te) may interfere with the permanganometric determination of selenium. In view of the fact that during the analysis the selenium separates out in the elemental form and is carefully washed free of impurities, these elements are only important in the initial stages of the analysis. Ferric iron interferes in the sense that for its reduction a considerable amount of sulfur dioxide is used up and, further, it can be precipitated together with selenium. Although it is not titrated by Mohr's salt** all the same, its color can interfere with the exact determination of the equivalence point during titration with permanganate. Divalent copper forms compounds with selenious acid which are sparingly soluble in water; copper can also be reduced to the cuprous state in acid solution, thereby using up some of the reducing agent. Chromium, arsenic, and antimony in the higher valence states, and other oxidizing agents, can also lead to excess use of reducing agent.

It is extremely important to eliminate interference from iron and copper which may be present in appreciable amounts in test materials. The behavior of arsenic and antimony is known.

Trivalent iron was reduced beforehand to the divalent state or complexed as the pyrophosphate. The high value of the acidity of the solution prevents deposition of univalent copper compounds and prevents reduction of tellurium. Arsenic and antimony in the reduced state remain in solution in the strong acid.

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* At this stage selenium is converted into $SeSO_3$ which is readily decomposed on diluting the solution to give elemental selenium with a red color.

** If divalent iron should be adsorbed, it may lead to results which are too high, since excess permanganate will be used up in the titration.

Selenium can be determined on the basis of this reaction by two methods. In the first instance, the selenium precipitate can be titrated directly with permanganate until the former dissolves and a weak rose color appears; in the second case one can immediately add excess standard permanganate solution to the selenium and titrate excess permanganate with oxalic acid or Mohr's salt.

In attempting to determine selenium by the first method, standard potassium permanganate solution was added to an acid solution containing the precipitate of elemental selenium (obtained by reduction with sulfur dioxide and separated from impurities) until the precipitate had dissolved completely and the solution acquired a rose color. The amount of selenium was calculated on the basis of the amount of permanganate used. The results obtained when this technique was used showed considerable variation, since complete solution of selenium as a compound with the higher valency could only be effected by using excess permanganate. The results obtained were accordingly far too high. When, on the other hand, titration was only carried up to the point where a weak rose color appeared, it was found that some of the selenium remained undissolved and the results obtained were far too low. When titration was carried out at elevated temperatures, the selenium precipitate dissolved more rapidly, but the results obtained were too high because of partial decomposition of permanganate. The first variant therefore had to be abandoned and the second variant was then tried. In this case the acid solution containing selenium in the elemental state was treated with excess standard permanganate solution, and the whole gently warmed. The selenium was completely oxidized and passed into solution. Excess permanganate was back titrated with a solution of Mohr's salt. Oxalic acid is not so suitable.*

Nevertheless, even when this second variant was used, the results obtained were still inaccurate and were far too high. The reason for this appears to be the fact that excess permanganate reacts with the ion of divalent manganese formed during the reaction to give $MnO(OH)_2$ or MnO_2, which react fairly slowly with Mohr's salt if the latter is not present in excess.

The second variant was therefore abandoned as well.

Completely satisfactory results were obtained when the following technique was adopted. To an acid solution containing the precipitate of elemental selenium was added excess standard potassium permanganate and the solution warmed gently (to avoid breakdown of permanganate) on a water bath until the selenium had dissolved completely. Excess of a standard solution of Mohr's salt was then added and the whole again gently warmed. Excess Mohr's salt was then titrated with the same solution of permanganate. Calculations were based on the total volume of permanganate and Mohr's salt used. The amount of selenium was determined from the difference between the number of equivalents of permanganate and Mohr's salt used up during titration.

On the basis of what has been said above and a number of other experiments, the following method was developed for determining selenium.

a) Determination of Selenium in Pure Solutions

Into a 10 ml centrifuge tube was placed 1 ml of a solution of sodium selenite containing 0.79-0.0079 mg selenium. 1 ml of concentrated sulfuric acid was added and the solution mixed. The solution was allowed to cool and then 1 ml of concentrated hydrochloric acid saturated with sulfur dioxide added and the whole mixed again. When elemental selenium ceased to separate out 1-2 drops of 5% barium chloride was added and the whole mixed again.**

The solution was centrifuged, and when the selenium was not completely precipitated another 1-2 drops of barium chloride was added; the solution was mixed again and centrifuged. When precipitation of selenium was complete, the solution was poured off the precipitate and the precipitate washed again by centrifuging with distilled water 4-6 times. The wash liquors were tested for chloride ions (chloride ions are the most difficult of the other ions to remove and could interfere later on with the determination). When the precipitates stuck together to form dense lumps, they were broken up by means of fine glass rod, which was then rinsed once or twice over the test tube with one or two drops of water. To the precipitate of elemental selenium washed in this way was added 1 ml of 2 N sulfuric acid and 0.1-0.2 g of potassium sulfate; the solution was then heated

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* Oxalic acid reacts with permanganate on heating to 70°; the reaction between permanganate and Mohr's salt does not require the application of external heat and proceeds rapidly.

** Barium chloride was added to coagulate the colloidal selenium. In addition, the barium sulfate formed in the reaction mixture prevents the selenium from forming dense lumps and facilitates washing.

Determination of Selenium in the Presence of Iron. During determination of selenium in the presence of trivalent iron, the latter was reduced with sodium thiosulfate, hydroxylamine, stannous chloride, etc. Nevertheless, for a number of reasons (decomposition of thiosulfate with liberation of sulfur in strongly acid solution, premature reduction of selenium, etc.) these reducing agents were abandoned. In subsequent experiments, therefore, interference from iron was avoided by complexing it.

Determination of selenium in solutions containing iron was carried out as follows. 1 ml of a solution containing 0.79-0.0079 mg of selenium and 0.02-0.20 g of iron was introduced into a centrifuge tube and 1 ml of concentrated sulfuric acid added, and the solution mixed. The mixture was allowed to cool; 1 ml of concentrated hydrochloric acid saturated with sulfur dioxide was then added and the whole mixed again. After 10-20 seconds, selenium separated out in the form of a red, amorphous powder. When separation of selenium was complete, 1-2 drops of a 5% solution of barium chloride was added, and after some time the whole was mixed. The solution was centrifuged, and, if the selenium had not completely separated out, another 1-2 drops of 5% barium chloride solution was added, the whole was mixed and centrifuged again. When deposition of selenium was complete, the solution was poured off the deposit and the latter washed twice with 2-3 ml lots of 2 N sulfuric acid, and then with 4-5 lots of distilled water. The wash liquors were tested for complete absence of chloride and ferric ions. During the washing operation the deposit was broken up into small pieces by means of a glass rod and stirred up with each succeeding fresh portion of wash water. The glass rod was finally rinsed over the tube with 1-2 drops of distilled water.

When the precipitate had been finally washed clean, 1 ml of 2 N sulfuric acid and 0.1-0.2 g of potassium sulfate were added to the tube and the mixture heated until complete solution of selenium was obtained. The subsequent procedure was the same as that described for determination of selenium in pure solutions of its salts.

TABLE 2

Microdetermination of Selenium by the Permanganate Method in Solutions Containing Copper

ml of 1.0 M $CuSO_4$ solution	Amount of Se in sample, mg		Difference in mg
	found	taken	
0.5	0.1585	0.1580	+0.0005
2.0	0.1595	0.1580	+0.0015
2.0	0.1580	0.1580	+0.0010
2.0	0.1692	0.1580	+0.0008
3.0	0.1580	0.1580	+0.0000
3.0	0.1586	0.1580	+0.0006

Relatively small amounts of iron (about 28 mg) do not affect selenium determination. Larger amounts (about 300 mg) lead to high results. Nevertheless, when the number of washings of the selenium precipitate with 2 N sulfuric acid was increased, the results improved significantly.

Determination of Selenium in the Presence of Copper. When selenium is determined in solutions which contain copper, the latter may lead to excess use of reducing agent during the process of depositing selenium in the elemental state. This, however, is not of essential importance. Of greater importance is formation of sparingly soluble compounds of uni- and divalent copper, as well as adsorption of copper ions by the amorphous selenium precipitate. Divalent copper ions do not show an essential effect on the results; this was established in the course of special tests. Compounds of univalent copper, on the other hand, lead to high results.

The high value of the acidity of the solution at the moment of precipitation of the selenium to a considerable extent depressed the content of copper in the precipitate of elemental selenium. Adsorption has hardly any effect on the results of selenium determination.

For the reasons just stated, selenium was determined in solutions containing copper by the same technique as that used when iron is present. Results of such determinations in the presence of copper are given in Table 2. The presence of as much as 0.19 g of copper does not really affect the results. The somewhat high values found can be explained by insufficient washing of selenium free from excess reducing agent.

Determination of Selenium in the Presence of Antimony. Pentavalent antimony can be reduced by sulfur dioxide to the trivalent state and thus lead to use of excess reducing agent; antimony does not interfere with the determination of selenium by means of permanganate and Mohr's salt. When the solution is not acid enough, trivalent antimony compounds hydrolyze with formation of a precipitate; this can lead to high results.

If, during reduction of selenium and its subsequent washing, the acidity of the solution is not high enough, practically no antimony gets into the precipitate and it consequently does not interfere with selenium determination.

The technique for determining selenium in the presence of antimony is identical to that used for selenium determination in the presence of iron. Results obtained for determination of selenium in the presence of antimony are given in Table 3. 0.010 g of antimony has no essential effect on the results.

Determination of Selenium in the Presence of Iron, Copper, and Antimony. Determination of selenium in the solutions containing iron, copper, and antimony is carried out in the same way as for solutions containing selenium and iron. The results obtained differ little from those obtained for determination of selenium in solutions of its pure salts.

TABLE 3

Determination of Selenium by the Permanganate Method in Solutions Containing Antimony

ml of 0.1 M $SbCl_3$ solution	Amount of Se in sample, mg		Difference
	found	taken	
0.2	0.1553	—0.1580	—0.0027
0.2	0.1610	+0.1580	+0.0080
2.0	0.1562	—0.1580	—0.0018
2.0	0.1578	+0.1580	—0.0002

3. Determination of Selenium by a Macro Method.

Selenium is deposited from acid solution by means of a saturated solution of sulfur dioxide in hydrochloric acid. The precipitate of elemental selenium is filtered off and washed, first with dilute acid, and then with distilled water. Filtration must be carried out through a glass crucible, since filter paper is not suitable because of its tendency to be oxidized by permanganate.

The precipitate on the glass filter is treated with excess standard potassium permanganate solution containing sulfuric acid until the selenium has dissolved completely. The filtrate is treated with excess standard Mohr's salt solution. Excess of the latter is titrated with permanganate.

The use of the method in practice has come up against a number of difficulties, chief of which is the necessity of using glass crucibles and the difficulty of dissolving the elemental selenium on the filter.

SUMMARY

A Permanganate method has been developed for the determination of small amounts of selenium. The method is based on preliminary precipitation of selenium from strongly acid solution by means of sulfur dioxide, followed by centrifuging or filtration of the precipitate and oxidation with excess permanganate. Tellurium does not interfere since it is not deposited at the high value of the acidity used. One hour is sufficient for carrying out four selenium determinations. It is possible by this method to determine selenium with an accuracy of up to 10^{-6} g in a sample; the method is three times more accurate than the permanganate method of determining selenium as selenious acid.

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METHODS FOR THE ISOTOPIC ANALYSIS OF WATER

3. A METHOD FOR THE COMPLETE ISOTOPIC ANALYSIS OF WATER BY DECOMPOSITION ON IRON

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The method [1,2] is based on passing the vapors of the test water through a layer of incandescent iron. The water thereupon decomposes to give hydrogen and ferric oxide. The ferric oxide is then reduced with hydrogen of standard isotopic composition. The vapors of the regenerated water are condensed and its density is measured by the drop method [3]. The increase in weight of the water obtained as compared with standard water is purely the result of the presence of heavy oxygen isotopes. Knowing the density of the water before decomposition and the density of the regenerated water, the content of deuterium in the test sample is established by difference. 0.3-0.5 ml of water is required for an analysis, while the accuracy of a determination is determined by the accuracy with which the density of the water can be determined by means of the drop method (0.02-0.05%).

The setup used for decomposing and regenerating the water is shown schematically in Fig. 1. Decomposition and regeneration is effected in quartz tube 12, which has a diameter of 15-18 mm and is 50-55 cm long and is packed with fully reduced iron. An electric furnace 11 which is fitted round the outside of the tube maintains a temperature of 400-500°. The top end of the tube is drawn out, cut evenly and connected by means of rubber tubing 10 to one of the limbs of a three way tap 8. The lower end of the quartz tube ends in a socket with a branch tube 14. A quartz test tube 15, inside which is fused a fine quartz tube, is fitted into the ground joint. The side tube of the socket 14 is connected through tap 17 to a vacuum pump; tap 18 serves for connecting to the atmosphere. A compact stopper 13, made from thick silver gauze (or fused, dense quartz filter) is fitted in the lower part of the quartz tube.

Regneration of the water is effected by means of electrolytic hydrogen from cylinder 5. The hydrogen throughput is measured by means of water rheometer 4. The hydrogen is freed from any oxygen contamination by passage through tube 2 containing palladinized silica gel kept at a temperature of 450°, and dried by means of calcium chloride contained in tube 6; tube 7 which contains cotton wool is included to hold back any $CaCl_2$ dust. In order to protect drying tubes 6 from water vapor coming from the rheometer during the time when the apparatus is not in use, a Bunsen valve 1 is used. By means of tap 8, pure dry hydrogen can be directed either into tube 12 containing iron or through the Bunsen valve 9 into the atmosphere.

Activated iron was prepared by reducing ferric oxide which was prepared as follows. Into a 5% aqueous solution of ferric nitrate was passed ammonia from a cylinder until precipitation of hydrated ferric oxide was complete; the precipitate was filtered off and washed with hot water until there was no further smell of ammonia; it was finally dried at 120°; the thick paste of hydroxide was squeezed through an opening 1·5 – 2 mm in diameter. The cylindrical pieces of material obtained in this way were first dried, and then calcined over a period of a few hours at 600-800°. The ferric oxide "wire" was broken up into lumps 4-5 mm long; they were then sieved free of dust and strewn into tube 12. Having connected the tube with the setup and switched on the heat, hydrogen was passed through at the rate of 150-200 liters/hour until the oxide was completely reduced, after which, for several hours, hydrogen was still passed through the tube (300-500 liters/hour) in order to blow out any iron dust.*

* That contamination was absent was verified by carrying out control tests with distilled water.

Before each test the apparatus was swept for 10-15 minutes with hydrogen at the rate of 200-250 liters/hour at 450° in order to reduce any ferric oxide which may have been accidentally formed or left in the tube. Decomposition and regeneration of water consists of three stages. In Figs. 2a, and 2b are shown the positions of tap 8 and test tube 15 during the various stages of the analysis.

1. Decomposition of the Water. 0.3-0.4 g of purified water, whose density has already been established, was poured into a clean dry test tube 15. The level of the water in the test tube was fixed near the lower end of the narrow tube. Tap 8 was fixed in position I (Fig. 2a) and test tube 15 was connected in the hydrogen flow to the tube packed with iron so that the ground joint was in the position shown in I (Fig. 2b), after which passage of hydrogen through the apparatus was stopped and tap 8 was turned to position II (Fig. 2a). The test tube was heated by means of a small electric hot plate 16 and the water evaporated. On passage of the water vapor through the hot iron, the water decomposed: the oxygen reacted with iron to form ferric oxide, while the hydrogen passed into the atmosphere through the Bunsen valve 9. After complete evaporation of test sample, tap 8 was turned to position III (Fig. 2a), while the test tube itself was rotated so that the opening in the socket coincides with that in the cone (position II, Fig. 2b).

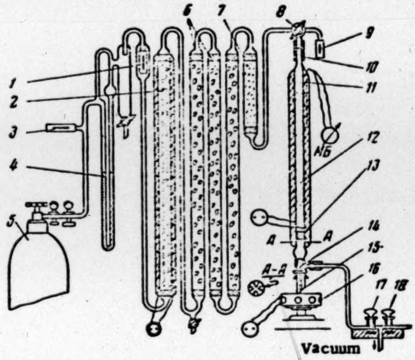

Fig. 1. Setup for decomposition and regeneration of water.

2. Removal of Traces of Undecomposed Water. Traces of undecomposed water which may accidentally remain in the apparatus were pumped out in the course of 10-15 minutes through tap 17. Duration of evacuation depends on the deuterium content, the higher the latter the longer the evacuation time. A small amount of undecomposed water with a high deuterium content can distort the results very strongly.

3. Regeneration of the Water. While the apparatus was still being evacuated, hydrogen was passed through from the cylinder into the apparatus, from which it was then let off into the atmosphere through tap 3; test tube 15 was cooled in a freezing mixture and tap 17 was closed. Liquid air was used for cooling, as well as mixtures of sodium chloride, or calcium chloride, and ice. Cooling with solid carbon dioxide was not used because of the possibility of contamination of test material with CO_2 vapors. Having switched off the vacuum pump and opened tap 18, tap 8 was turned to position I (Fig. 2a). Tap 17 was then immediately opened, as a result of which hydrogen started to pass through the layer of oxidized iron, thereby reducing it back again and forming water. The water vapor was condensed in test tube 15, while excess hydrogen passed through taps 17 and 18 to the atmosphere. Reduction of ferric oxide took 5-10 minutes when the hydrogen throughput was 150-250 liters/hour. The test tube was then placed in warm water, after first of all turning the ground joint to position I (Fig. 2b). When the ice had melted, the test tube was taken off the ground joint and, without further purification was placed in a dropper for determining the density by the drop method.

As experiment showed, on decomposing water with a high deuterium content, some of the deuterium still remained in the regenerated water and this leads to high values of the O^{18} concentration. Consequently, during analysis of such water, the regenerated water was again decomposed and after careful evacuation of the apparatus the water was regenerated for the second time. This repeat regeneration gave the correct results for test water containing deuterium concentrations approaching 100% in which the O^{18} concentration was not more than 0.5%.

In cases where analysis of samples with a low concentration of O^{18} was followed by analysis of samples with a higher O^{18} content (1% and higher), low results were obtained; and, vice-versa, on switching from samples with high concentration to samples with low O^{18} concentration, high results were obtained. This is the result of incomplete reduction of ferric oxide.

In order to avoid such errors, the apparatus was "trained" by making several replicate analyses of the same sample until constant results were obtained.

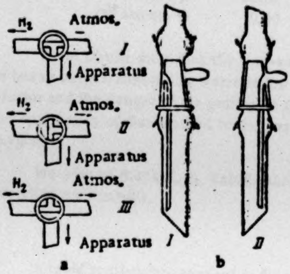

Fig. 2. Positions of tap 8 and test tube 15 during the various stages.

During analysis of samples with high O^{18} contents the hermetical sealing of the apparatus was of great importance, so as to avoid traces of atmospheric oxygen getting into the tube containing the iron.

The molecular weights and molecular volumes of H_2O^{18} and D_2O^{16} are very close; consequently, during calculation of the results, the relationships between density and molecular concentrations for these two isotopic forms of water are regarded as being practically the same, and the presence of H_2O^{17} is ignored.

We give below some examples illustrating the results (I) obtained by means of the method just described, and a comparison of these with results obtained by analyses carried out on the basis of normalization of the isotopic composition of oxygen to magnanese dioxide [4].

Sample No. 1: $D + O^{18}$ = 1.58 atomic %

I: 0.50; 0.52; 0.54; 0.50 Mean 0.52 atomic % O^{18}
II: 0.54; 0.54; 0.56; 0.56 Mean 0.56 atomic % O^{18}

Thus, at concentrations of O^{18} atomic % = about 0.5 the analytical results agree within the limits of accuracy of the drop method. At higher O^{18} concentrations, the analytical results obtained only agree after preliminary "training" of the apparatus for the iron-vapor method.

Sample No. 2: $D + O^{18}$ = 10.28 atomic %

I* (0.92; 1.08; 1.18; 1.20); 1.30; 1.32 1.32; 1.28; Mean 1.30 atomic %
II 1.27; 1.27; 1.27; 1.27; 1.24; 1.27 1.32; Mean 1.27 atomic %

In addition, here are the mean results of analysis of three samples of water, in which determinations were made in parallel by the two methods:

Sample number	3	4	5
Total $D + O^{18}$ atomic %	0.33	0.70	3.50
I:	0.21	0.38	0.88
II:	0.24	0.35	0.93

Below are given results which characterize the applicability of the iron-vapor method for determining the concentration of heavy oxygen isotopes in water with high deuterium content.**

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* Results after double decomposition and regeneration of the water.

** Total concentration was determined by a pycnometric method. The water was decomposed and regenerated twice.

Sample number	6	6	6	7	7	8	8
Total D + O^{18} atomic %	99.51	99.51	99.51	99.89	99.89	99.93	99.93
O^{18} atomic %	0.10	0.08	0.09	0.06	0.06	0.08	0.08

These results show that the iron-vapor method can be successfully used for determining the concentration of heavy oxygen isotopes in water at low concentrations of these isotopes. The necessity of "training" the apparatus and the danger of air getting in through the dry ground joint to the tube containing the iron complicates the application of this method to the analysis of samples which have a high content of the heavy isotopes of oxygen.

We wish to thank K. P. Voloshenko for carrying out some of the analyses and E. A. Yakovleva for superintending the analysis.

SUMMARY

A rapid semi-micro method is described for complete isotopic analysis of water. This method, in conjunction with the drop method of determining density, permits separate determination of the heavy isotopes of oxygen and hydrogen (deuterium) in samples containing any amount of deuterium.

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A SIMPLIFIED FLOTATION METHOD FOR MEASURING LIQUID DENSITY

(SUSPENDED FLOAT METHOD)

S. M. Karpacheva, A. M. Rozen, L. I. Samsonova, and S. N. Stepanova*

The flotation temperature method of measuring liquid density is widely used in physicochemical research; in particular, for the isotopic analysis of water [1, 2]. This method is based on a comparison of the flotation temperatures of a float** t_f in the test and standard water (difference in densities is calculated on the basis of Δt_f). To determine the flotation temperature accurately, the rate $\underline{v}$ at which the float moves at 4-5 temperatures near t_f is measured; the latter is found by interpolation along the t-v graph (t_f corresponds to zero rate of movement of the float). Measurements are carried out with careful control of temperature (an accuracy of not less than 0.001°); a cathetometer is used for observation of the movement of the float and for observation of the temperature measured with a Beckmann thermometer.

Water samples were given a preliminary purification by repeated distillations.

The flotation method allows the density of water to be measured with a high degree of accuracy ±0.5γ [1], but requires rather complicated apparatus for accurate thermostating, and also takes a long time to carry out (thermostating and measurement of the rate of motion of the float at one temperature takes 20-30 minutes, so that one complete determination takes 2-3 hours).

In the present article a description is given of a simple and accurate variant of the flotation method, which is based on another method of measuring the flotation temperature.

15-20 determinations can be carried out on one apparatus in one day.

The method developed is based on direct determination of the flotation temperature.

Numerous experiments showed that the temperature at which float movement ceases can be determined accurately and comparatively rapidly. The only prerequisites for this is a good thermostat with good heat insulation (with a low temperature rate) and a micro-heater by means of which the temperature can be changed slowly enough by 0.001-0.003°/minute. (Initially the temperature is changed more rapidly, but with the slowing down of float movement, temperature changes are also slowed down.) When the float comes to a stop the temperature is kept constant for several minutes; subsequently, as a check, the temperature is first increased by 0.001-0.002° and then lowered by the same amount. If the flotation temperature has been established correctly, then in the first instance the float will start to sink and in the second instance will float upwards. Next, the test tube plus float are carefully shaken up in the thermostat and the flotation temperature determined again. For normal operations, deviations should not exceed 0.001°.

All these operations can be carried out in 20-30 minutes after some practice.

During all the test period test tube and float are kept at a temperature very close to the flotation temperature, so that one can be assured that thermal equilibrium is achieved.

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* The method described was developed by the first three authors. The work described in paragraphs 4 and 5 was carried out by A. M. Rozen and S. N. Stepanova.

** The flotation temperature is the temperature at neutral equilibrium when the float neither sinks nor comes to the surface; its average density is equal to the density of the liquid.

Thermostat Construction

The thermostat shown schematically in Fig. 1 was constructed for measuring flotation temperature. The main vessel 3 which is of glass (capacity 6 liters) is placed in an insulating mantle 1; the insulating material 4 (glass wool) is 50 mm thick.

The lid of the thermostat 2 is similarily insulated. There are two breaks in the insulation; one (5) for observation of the test tube containing the float, the other (on the other side) for illumination.

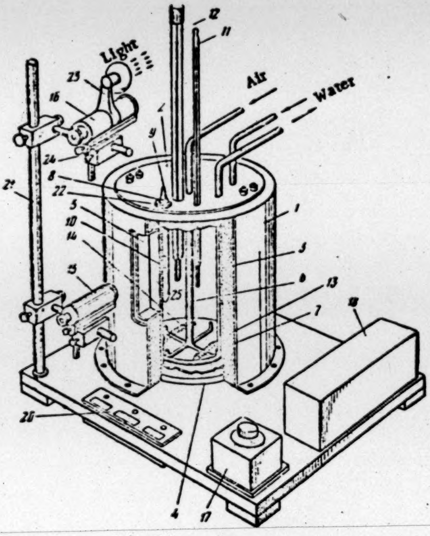

Fig. 1. Thermostat.
1) body of the thermostat; 2) thermostat lid; 3) glass vessel; 4) thermostat base; 5) frame; 6) air-lift; 7) cooler; 8) test tube; 9) hood; 10) float; 11) Beckman thermometer 3-5°; 12) 100° thermometer with 0.2 scale divisions; 13) heater No. 1; 14) heater No. 2; 15) eyepiece for observing float; 16) eyepiece for observing Beckman thermometer; 17 rheostat; 18) 220/17 v transformer; 20) switch; 21) stand for support of optical apparatus; 22) support ring; 23) base of lamp for illuminating the float; 24) support for optical apparatus; 25) inspection hole.

For coarse adjustment of temperature, the thermostat is provided with a large heater – 13, (rated at 300 watts) capable of heating the water in the glass vessel through 0.5° in 1 minute (connected directly from the mains). The micro-heater 14 mentioned above, which has a wattage of 20 watts and is used for determining the flotation temperature, is fed through a transformer 18 at a voltage of 17 v; the micro-heater circuit includes a regulating rheostat 17 with a resistance of 50-60 Ω, whereby the power supplied to the heater can be altered from 20 to 0.75 watts (the smallest power supplied to the heater is sufficient for heating the water in the thermostat through 0.0015° per minute).

The thermostat is also supplied with a cooling coil 7 through which tap water is passed, and with an air stirrer 6. Special tests showed that the air stirrer ensures sufficiently good equal temperature distribution, while its construction is considerably simpler than that of a mechanical stirrer. Further, the air stirrer serves as an additional means of regulating the temperature, and can be used for rapid cooling of the thermostat in the case of accidental overheating ; thus it helps maintenance of the requisite temperature in a steady state during measurements (the air supply is controlled by means of a reducer and a valve).

The combination of micro-heater, and water and air cooling, permit one to control the temperature manually (the micro-heater by means of the rheostat) to the accuracy of 0.001° for 10-30 minutes, necessary for carrying out measurements; there is no need for special controlling devices.

Measurements are carried out at room temperature. By carrying out measurements near the temperature at which water has its maximum density it is possible to increase accuracy of determination considerably; this of course is only true in combination with particularly accurate methods of purifying test samples.

Heaters, the cooling coil, and the stirrer are arranged on the bottom and are fixed to the lid of the thermostat; the latter has openings for observation of the measuring test tube and the thermometers (Beckman [11], and an ordinary thermometer with scale divisions of 0.1° [12]).

The quartz test tube 8 and the float 10 do not differ in constructional details from those normally used [1]; the test tube is provided with a cap 19 (see also Fig. 2). The tail of the float must be fused off after grinding ; otherwise the rough tail surfaces may easily adsorb contamination, and the flotation temperature of the float in standard water changes rapidly.

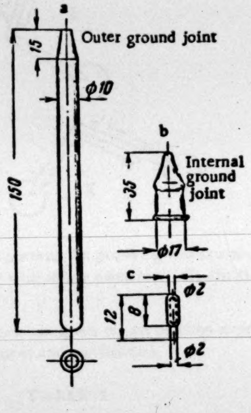

Fig. 2. Test tube and float for measuring liquid density. a) test tube (quartz); b) cap (quartz); c) float (fused quartz).

The cathetometers for observing float movement (15) and temperature readings (16) are fixed on a special stand. The first cathetometer should preferably have a focal length of 70 + 100 mm.* The reason for this is as follows. For differences of more than 4-5° between room and thermostat temperatures, it is necessary for accurate measurements to thermally insulate the inspection hole in the thermostat. For this purpose it is necessary to introduce a second observation window, while the test tube should not be closer than 40 mm to the observation window.

Preparation of Test Samples and Apparatus

The accuracy of isotopic analysis on the basis of density measurements depends to a large extent on the content of impurities in test samples; consequently, considerable attention must be given to the purification step [1]. In Fig. 3 are shown the apparatus we used; they are distinguished by the fact that they can be adapted both for oxidation (boiling under reflux, position No. 1) and for distillation (position No. 2). For purifying samples containing more than 0.5% of heavy isotopes, the apparatus was supplied, in addition, with a side tube fitted with a Bunsen valve (to prevent contact of test samples with the outer air).

Purification was originally carried out in four stages: 1) oxidation with permanganate in acid media followed by distillation; 2) ditto in alkaline media; 3) distillation without addition of reagents, and rejection of fraction 3; 1;*4) distillation in a quartz apparatus immediately before measurements. Each operation was carried out in individual, carefully cleaned and steamed out apparatus.

Subsequently it was found that there is no need to carry out each operation in separate apparatus. The first three operations can be carried out without harm to the quality of the purification in one condenser and combination of four flasks (the receiver is used as the starting flask for the next operation; this of course means special fitting ground joints). By using one apparatus like this, preparation and purification time is cut down considerably. Further, it was established that contact with outside air during distillation and steaming out of the flasks distorts the results of the density measurements at heavy isotope contents of greater than 0.5%.* Thus, during purification of samples containing 1-3% of D or O^{18} in a steamed out flask, the scatter in the results amounted to about 10γ. This scatter decreased to ± 1.5 − 3γ after fitting Bunsen valves, while steaming out was replaced by rinsing with test water and subsequent drying. The undesirable effects produced by steaming out were probably caused by adsorption of moisture by the apparatus walls. In subsequent experiments the steaming out stage was omitted, and during preparation of weakly concentrated samples the vessel was rinsed with twice distilled water which had an electrical conductivity of not more than $1 \cdot 10^{-6}$ mhos/cm.

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* As in original – Editor's note.

Completness of purification was controlled on the basis of the electrical conductivity of the samples; the conductivity should not exceed $1.5\text{-}2 \cdot 10^{-6}$ mhos/cm. It was found that, other conditions being equal, the quality of purification depends on the fit of the ground joints. Loose fit of the joints led to loss of some of the test sample and to distortion of the isotopic composition as the result of fractionation (it should be noted that the fractionating columns shown in Fig. 3 give bottoms in amounts approximating the amount of liquid distilled).

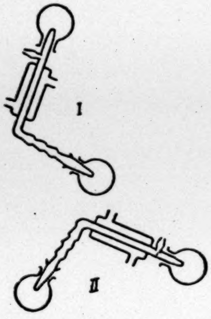

Fig. 3. Apparatus for purifying test samples.
I) boiling with reflux condenser; II) distillation.

Test tube and float were kept for 24 hours in hydrochloric acid before use; they were then boiled in a solution of sodium carbonate and washed with chromic acid, followed by water and twice distilled water; finally test tube and float were steamed in twice distilled water for 2-3 hours. After steaming out test tube and float meant for measuring light samples, they were rinsed with twice distilled water, while in the case of heavier samples they were washed with water of approximately the same concentration as the water which is going to be measured. Before measurement the test tube was rinsed with test water. At the end of a working day the test tubes were left covered with water of similar concentration or with twice distilled water.

Checking the Method

The technique described has been checked in the course of many years on several thousand samples. In most cases measurements were carried out in parallel in two thermostats; purification was also carried out in parallel.

Below are given results of some experiments which were made specially for determining errors during measurement and purification.

TABLE 1

Measurement of Flotation Temperature of a Sample Containing Less than 100γ of Heavy Isotope

	1	2	3	4	5	6	7	8	9	10
Flotation temperature	0.383	0.382	0.383	0.383	0.383	0.383	0.382	0.384	0.383	0.383

Mean value − 0.383
Mean square deviation − 0.0006

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* One should bear in mind that D_2O is hygroscopic even at concentrations of about 1%.

TABLE 2

Measurement of t_f of a Sample Containing Less than 1000 γ

	1	2	3	4	5	6	7	8	9	10
Flotation temperature	2.527	2.525	2.525	2.525	2.525	2.525	2.525	2.525	2.525	2.525
Heavy isotope content in γ	556.9	556.4	556.4	556.4	556.4	556.4	556.4	556.4	558.4	556.4

Mean value 556.4

As can be ssen from Table 1 and 2, the scatter during measurement of the flotation temperature amounts to about 0.001° and within the limits indicated, is practically independent of the concentration of heavy isotopes in the water. Thus measurements of the flotation temperature on a KRS thermostat corresponds to 0.2γ on a density basis.

TABLE 3

Effect of Purification on Results of Measurements

Sample number	No. of replicate purification	Result of replicate measurements	Mean value for one purification	Mean value for duplicate purifications
1	1	98.7	98.8 ±0.1	98.8±0.4 =0.276
		98.9		
	2	99.1	99.2 ±0.1	
		99.3		
	3	98.4	98.5 ±0.1	
		98.6		
	4	98.8	98.9 ±0.1	
		99.0		
2	1	261.4	261.4	261.6±0,25
		261.4		
	2	261.8	261.85±0.05	
		261.9		
3	1	268.2	268.05±0.15	267.3±0.8
		267.9		
	2	266.6	266.5 ±0.1	
		266.4		

The overall accuracy of an analysis is somewhat less and is determined mainly by the quality of the purification. The effect of the latter on the results is illustrated in Tables 3-5.

As the results in Table 3 show, the scatter of replicates does not exceed ± 0.15γ, while for parallel purification the scatter amounts to ± 0.8γ. Thus, analytical accuracy is determined by the quality of purification.

Practice showed that for isotope content up to 100 γ, analytical accuracy amounts to about ±0.5γ (when purification is carried out carefully — 0.3γ).

At concentrations of about 1500 γ, analytical inaccuracy increases, because of fractionation during purification, to 1.5γ; the following results were obtained: 84.4; 84.4; 85.4; 85.6; 82.7; 83.7; 83.7; 84.1γ, which gives a mean of 84.15 ± 1.5 γ (mean square deviation $\sqrt{\Delta^2} = 1.1$).

TABLE 4
Verification of Reliability of the Method

Calculated excess concentration	Concentration measured (γ)				
	1 purification	2 purification	3 purification	4 purification	5 purification
954.7	955.4	953.4	952.3	956	955.3

Mean value 954.5 γ; $\sqrt{\Delta^2} = 1.5$.

We found that at contents of heavy isotopes ranging from 0.5 to 5% an accuracy of about 0.1% of the measured value can be achieved when purification is carried out carefully.*

Special experiments were carried out to establish the reliability of the method. Water containing 74.48% D_2O (according to pycnometric measurements) was diluted gravimetrically, after which measurements of the density were carried out by the method described above.

Results of these measurements are given in Table 4.

Results of similar tests with a sample containing less D_2O (original sample 3.14% D_2O) are given Table 5.

TABLE 5

Calculated excess concentration	Measured concentration					
	1 purification		2 purification		3 purification	
	1 meas.	2 meas.	1 meas.	2 meas.	1 meas.	2 meas.
61.6	61.4	61.4	61.6	61.5	61.9	61.8

Mean value 61.6 γ.
Mean square deviation $\sqrt{\Delta^2} = 0.19\gamma$.

The good agreement obtained between calculated and experimental results indicates the absence of any systematic error when this simplified flotation method of measuring density is used; thus the scatter of the experimental results determines their accuracy in practice.

SUMMARY

1. A simplified variant of the flotation method of determining density has been developed; it is based on direct determination of flotation temperature (suspended float method).

2. The thermostat specially constructed for carrying out this method is very simple (a mechanical stirrer is replaced by an air stirrer and there is no need for a heat regulator) and can be made in any laboratory.

A density measurement by the suspended float method in the thermostat takes 20-30 minutes.

3. The accuracy of determination of the flotation temperature by the method described is about 0.001° (which corresponds to 0.2-0.25 γ in terms of density). The accuracy of density measurement as a whole is determined by the quality of purification: at concentrations of heavy isotopes of up to 100 γ, the accuracy ranges from ± 0.3 to ± 0.5 γ, while for concentrations of D_2O ranging from 0.5 to 5%, it is about 0.1% of the measured value.

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* In any case, during comparative measurements, the absolute values of the density may be less accurate because of the necessity of fitting more than one Beckman thermometer (the 5° scale on a Beckman thermometer corresponds to a density range of about 1000γ).

A PHOTOMETRIC METHOD OF DETERMINING THE VAPORS OF CERTAIN ALKYL- AND ARYLCHLOROSILANES IN AIR

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The wide use of silico-organic monomers of alkyl- and arylchlorosilanes in industry, considering their toxicity, makes it necessary to develop accurate and rapid methods for their determination. Existing methods for the determination of alkylchlorosilanes in air [1,2], are based on decomposition of the material with subsequent determination of silicon dioxide. Qualitative reactions for alkyl- and arylchlorosilanes have also [3] been found which do not necessitate preliminary mineralization; we have used these reactions for quantitative determinations. The reactions are based on formation of characteristic precipitates with a red-orange color during interaction of alkyl- and arylchlorosilanes with a solution of tetramethylaminobenzophenone in aniline, and on the formation of a violet-red color during interaction of phenylchlorosilanes with anhydrous aluminum chloride and a benzene solution of tetramethyldiaminobenzophenone. The mechanism of the reactions has not been clarified.

According to Kreshkov and Bork [3], during interaction with an aniline solution of tetramethyldiaminobenzophenone, there is formed phenylauramine hydrochloride $[(CH_3)_2NC_6H_4]_2{=}NC_6H_5 \cdot HCl$ which is adsorbed by the reation product of alkylchlorosilane with aniline, and colors the latter red. As for the reaction with $AlCl_3$, Kreshkov and Bork point out that tetraphenylsilane and phenylchlorosilanes react with anhydrous aluminum chloride as follows: $(C_6H_5)_4Si + AlCl_3 \rightarrow (C_6H_5)_3SiCl + C_6H_5AlCl_2$; $(C_6H_5)_3SiCl + AlCl_3 \rightarrow (C_6H_5)_2SiCl_2 + C_6H_5AlCl_2$, etc.

Since neither arylchlorosilanes nor $SiCl_4$, which are the end products of these reactions, give a violet-red color with a benzene solution of tetramethyldiaminobenzophenone, it may be concluded that the latter reacts with $C_6H_5AlCl_2$ which is obtained on heating tetraphenylsilane $[(C_6H_5)_4Si]$ or phenylchlorosilanes with aluminum chloride. The limit of identification of alkyl- and arylchlorosilanes is 15 mg in a drop of solution.

We carried out some work with the aim of establishing the optimum conditions for determining small amounts of methyltrichlorosilane CH_3SiCl_3, dimethyldichlorosilane $(CH_3)_2SiCl_2$, and ethyltrichlorosilane $C_2H_5SiCl_3$, diethyldichlorosilane $(C_2H_5)_2SiCl_2$, and phenyltrichlorosilane $C_6H_5SiCl_3$. It was found that the best organic solvents for preparing a series of standard solutions of these materials were petroleum ether and carbon tetrachloride. Solutions of the test alkyl- and arylsilanes in the solvents indicated react with a 2% solution of tetramethyldiaminobenzophenone to give characteristic precipitates. At high concentrations of 5 mg/ml and higher there are formed precipitates of red-orange color; at concentrations of hundredths and thousandths of a milligram in 1 ml the solution is colored yellow-orange. Under these conditions the color intensity of the solutions increases in proportion to the concentration. It was established that color intensity increases with time; this interferes with accurate colorimetric determination. It was established at the same time that when petroleum ether is added to the test solution, a protective layer is formed which prevents an increase in color.

From 0.005 to 0.1 ml lots of a standard solution of ethyltrichlorosilane in carbon tetrachloride containing 10 mg of test material per ml were introduced by means of a 0.1 ml micro-pipet into colorimetric microtest tubes. The solution was made up to 0.5 ml with petroleum ether added from a Shilov buret; finally, to each was added 0.5 ml of a 2% solution of tetramethyldiaminobenzophenone in aniline. The contents of the tubes were mixed and their colors measured after 30 minutes.

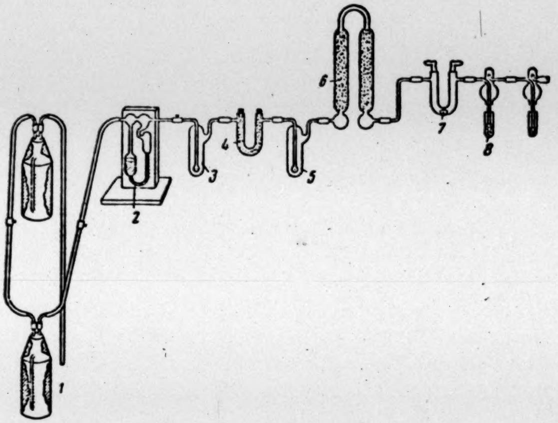

Fig. 1. Setup for measuring out alkyl- and arylchlorosilanes.
1) aspirator; 2) rheometer; 3) Petri buffer absorber; 4) U-tube filled with activated charcoal and glass wool for absorbing any kerosene vapors from the rheometer; 5) Petri buffer absorber; 6) calcium chloride tube; 7) U-tube with alkyl- or arylchlorosilanes; 8) absorption apparatus.

When colorless, freshly distilled aniline is used, the limiting amount of silico-organic compounds which can be determined is 0.01 mg in 1 ml. Having decided on the optimum conditions for determining alkyl- and arylchlorosilanes by means of an aniline solution of tetramethyldiaminobenzophenone, we carried out some experiments to establish the possibility of using the reaction with aluminum chloride and a benzene solution of tetramethyldiaminobenzophenone. These experiments showed that depending on the concentration of alkyl- and arylchlorosilanes, the solution may have colors ranging from yellow-orange (hundredths and thousandths of a milligram/ml) to a violet red (2-5 mg/ml). The color which is formed during interaction with alkylchlorosilanes disappears after 15-30 minutes, while phenyltrichlorosilane, under the same conditions gives a color which is stable for 3-4 hours. This means that one can determine phenyltrichlorosilane in the presence of the alkylchlorosilanes indicated above.

The following optimum conditions are recommended for determining phenyltrichlorosilane: various amounts of phenyltrichlorosilane (0.01 to 1 mg) dissolved in benzene are placed in micro colorimetric tubes. The volume is made up to 0.5 ml with benzene from a Shilov buret, and about 10 mg of anhydrous aluminum chloride added. The tubes are shaken and then stood for 30 seconds in a water bath heated to 85°; they are withdrawn at the end of this time from the bath and cooled; 0.5 ml of a 3% saturated solution of tetramethyldiaminobenzophenone in benzene is then added to each tube. The tubes are replaced in the bath, still at the same temperature, for another 30 seconds, and the colors measured after 15 minutes.

Experiments to find a method of absorbing alkyl- and arylchlorosilanes from the air were carried out as follows (Fig. 1): into a U-tube 5 cm long and 1 cm diameter and fitted with ground stop cocks were introduced known amounts of a standard solution of alkyl- and arylchlorosilane. The vapors of the silico-organic compound were blown by means of a dry air stream into 2 modified Polezhaev absorption apparatus (Fig. 2), which serve simultaneously as absorbers and tubes, each containing 0.5 ml of a 2% solution of tetramethyldiaminobenzophenone in aniline and 0.5 ml benzene. When a test was finished the volume was made up with benzene to the original volume and the color compared with that of a standard scale. It was established that on drawing the test air through the apparatus at the rate of 30 liters/hour, alkyl- and arylchlorosilanes were completely absorbed in the first absorber.

It is clear from Table 1 that the vapors of the silico-organic compound are efficiently absorbed; the relative experimental error amounts to 20%.

We recommend the following method for taking air samples and for determining alkyl- and arylchlorosilanes: through two absorbers each containing 0.5 ml of a 2% solution of tetramethyldiaminobenzophenone in aniline and 0.5 ml of petroleum ether or a 40-100 benzine fraction, air is sucked at the rate of 0.5 liter/minute.

For determining phenyltrichlorsilane by means of aluminum chloride and a benzene solution of tetramethyldiaminobenzophenone, the same absorbers are used but with the first absorber containing 1 ml and the second 0.5 ml of benzene. When air is being drawn through, the absorbers should be cooled and the temperature kept not much higher than +6°. After taking the air samples, the volume of the liquid in the absorbers is made up to the original volume with benzene; the color intensity of the alkyl- and arylchlorosilanes is compared after 30 minutes with a standard scale prepared as follows: 0.005-0.1 ml lots of a standard solution of alkyl- or arylchlorosilane in carbon tetrachloride (10 mg/ml) are introduced into colorimetric tubes by means of a 0.1 ml micro-pipet. The volume of the solution is made up to 0.5 ml with benzene measured from a Shilov buret, and 0.5 ml of a 2% solution of tetramethyldiaminobenzophenone is then added to each tube.

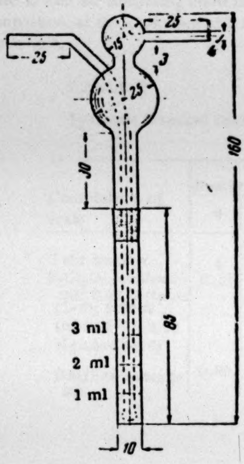

Fig. 2. Micro-absorber.

TABLE 1

Absorption of Ethyltrichlorosilane by Means of a 2% Solution of Tetramethyldiaminobenzophenone in Aniline

$C_2H_5SiCl_3$ taken, in mg	$C_2H_5SiCl_3$ found		Error, in %
	in mg	in %	
0.05	0.04	80.0	—20.0
0.10	0.09	90.0	—10.0
0.20	0.20	100.0	0
0.30	0.30	100.0	0
0.40	0.40	100.0	0
0.50	0.50	100.0	0
0.60	0.60	100.0	0
0.80	0.70	87.5	—12.5
1.00	0.80	80.0	—20.0
2.00	1.70	85.0	—15.0

From a hygienic point of view the rate of hydrolysis of substituted chlorosilanes as a function of the moisture content of the surrounding air is of considerable interest. The following experiments were carried out in order to determine this rate of hydrolysis: through solutions of alkyl- and arylchlorosilanes contained in U-tubes, air at a relative humidity of 30-40% was drawn for various time intervals; undecomposed chlorosilanes were then determined colorimetrically by the method described above. In the course of the first 5-10 minutes while the air was being drawn through, the substituted chlorosilanes were not hydrolyzed. On blowing very damp air through, alkyl- and arylchlorosilanes hydrolyzed in the first 2-5 minutes to the extent of 80-100%. During production of silico-organic polymers, alkyl- and arylchlorosilanes may be accompanied by the ethyl ester of orthosilicic acid and by silicon tetrachloride.

It was found that ethyl orthosilicate does not interfere with the determination described above at any concentration. Silicon tetrachloride interferes with determination by means of an aniline solution of tetramethyldiaminobenzophenone, but does not — in amounts up to 3 mg — affect determination by means of anhydrous aluminum chloride and a benzene solution of tetramethyldiaminobenzophenone.

Since the color intensity of the standard scale made up from alkyl-and arylchlorosilanes with a 2% solution of tetramethyldiaminobenzophenone in aniline increases with time, then in order to get more accurate results, and also to cut down on time and improve the analytical technique, two synthetic standard scales have been developed; these are potassium dichromate solutions of various concentrations (Table 2 and 3). The first scale is used for comparing color intensities for samples at the end of one hour, while the second is used for comparison at the expiration of 3 hours from the time when the sample was taken. The scales are stable for one month.

TABLE 2

Synthetic Standard Scale

Composition of scale	Number of mg of alkyl-and arylchlorosilanes to which it corresponds									
	0	0.05	0.10	0.20	0.40	0.60	0.80	1.00	2.00	4.00
Tube number	1	2	3	4	5	6	7	8	9	10
$K_2Cr_2O_7$ solution in ml: 0.02 N (tubes (1-4); 0.20 N (tubes 5-7); 2.00 N (tubes 8-10)	0.20	0.32	0.50	0.67	0.23	0.44	0.89	0.16	0.42	1.00
Distilled water in ml	0.80	0.68	0.50	0.33	0.77	0.56	0.11	0.84	0.58	0

TABLE 3

Synthetic Standard Scale

Composition of scale	Number of mg of alkyl- and arylchlorosilanes to which it corresponds									
	0	0.05	0.10	0.20	0.40	0.60	0.80	1.00	2.00	4.00
Tube number	1	2	3	4	5	6	7	8	9	10
$K_2Cr_2O_7$ solution in ml: 0.02 N (tubes (1-2); 0.20 N (tubes 3-5); 2.00 N (tubes 6-9); 3.00 N (tube 10)	0.26	0.82	0.16	0.25	1.00	0.21	0.43	0.52	1.00	0.87
Distilled water in ml	0.74	0.18	0.84	0.75	0	0.79	0.57	0.48	0	0.13

The colorimetric method developed enables one to determine hundredths and thousandths of a mg of methyltrichlorosilane, dimethyldichlorosilane, ethyltrichlorosilane, diethyldichlorosilane, and phenyltrichlorosilane in 1 liter of the air of industrial enterprises in the course of 5-10 minutes.

SUMMARY

1. A photometric method has been developed for the determination of small amounts of the vapors of certain alkyl- and aryl- substituted silico-organic monomers of the type R_nSiCl_{4-n}: it is based on the formation of a yellow-orange color (hundredths, tenths of mg) and a red-orange (several mg) color during the interaction of alkyl- and arylchlorosilanes with a 2% solution of tetramethyldiaminobenzophenone in aniline.

and the formation of a yellow-orange color for hundredths and thousandths of a mg during interaction of phenyltrichlorosilane with anhydrous aluminum chloride and a 3% saturated solution of a benzene solution of tetramethyldiaminobenzophenone.

The sensitivity of the method is 0.01 mg/ml.

2. A technique has been developed for taking samples of alkyl- and arylchlorosilanes for the purpose of determining their vapors; they are sampled in two specially constructed absorbers, each of which contain 0.5 ml of a 2% solution of tetramethyldiaminobenzophenone in aniline and 0.5 ml of benzene; in another variant, one absorber (the first in the chain) contains 1 ml of benzene, while the other contains 0.5 ml of benzene, for determination of the vapors of phenyltrichlorosilane.

3. Ethyl orthosilicate and hydrogen chloride vapors do not interfere. Silicon tetrachloride interferes in the reaction involving a 2% solution of tetramethyldiaminobenzophenone in aniline, but does not affect – in amounts up to 3 mg – the reaction involving anhydrous aluminum chloride and a benzene solution of tetramethyldiaminobenzophenone.

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DETERMINATION OF AMMONIA AND VOLATILE ALIPHATIC AMINES BY AN INDIRECT POLAROGRAPHIC METHOD

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Photometric and nephelometric determination of ammonium salts [1,2] and nitrogen [3] by means of Nessler's reagent have been described by several authors. The method is highly sensitive [4]. The limit of identification is 0.25 mg NH_4^+ in 5 ml. At concentrations of the ammonium salts approaching the limiting dilution, after addition to the Nessler reagent, the solution develops a more or less observable yellow color which obeys Beer's law, and is determined by the formation of Millon's base. At high ammonium salt concentrations, a turbidity, or colloids appear which prevent accurate photometric determination and require special conditions for nephelometric measurements. The use of protective colloids has not yet yielded satisfactory results. A more successful attempt at preventing the development of the undesirable turbidity has been described by Slavik and Nichales [3]. During standardization of the method for determining nitrogen, Slavik and Nichales established suitable dilutions both for the reaction mixture formed after the Kjeldhal stage and for the Nessler reagent itself, for certain nitrogen content ranges. They state that on using this method and observing a definite concentration range for the sulfuric acid used for the combustion, they succeeded in completely preventing the appearance of a turbidity and got a linear calibration curve. The intensity of the color of the solution, however, changes somewhat with time; consequently, colors are measured after a definite time interval. The facts enumerated above led us to try to develop an indirect method of determining ammonia by means of Nessler reagent on the basis of a polarographic determination of mercury.

A large amount of data has been published relating to the polarographic behavior of mercury [5–9, 13–18, 21–42, 44–45].

Kolthoff and Miller [19,20] established the two electron polarographic reduction of univalent mercury ions, and obtained waves identical with the waves of divalent mercury; they explain this by the rapid establishment of the equilibrium $Hg^{2+} + Hg \rightleftarrows 2Hg_2^{2+}$ on the surface of the drop electrode. On the basis of the equilibrium constant (approximately 100) they affirm that the Hg^{2+} ion concentration amounts to only 1% of the concentration of Hg_2^{2+} ions. During a study of the reduction of complex ions of divalent mercury, HgI_4^{2-} or $Hg(S_2O_3)_2^{2+}$, in excess of KI or $Na_2S_2O_3$ respectively, the reversibility of the electrode reaction was established. The anode waves of $S_2O_3^{2-}$ or SO_3^{2-} also correspond to the formation of complex ions $Hg(S_2O_3)_2^{2-}$ or $Hg(SO_3)_2^{2-}$ with divalent mercury. Schwarz [18] determined mercury by reduction of the complex anion HI_4^{2-} in a mixture of potassium iodide with sodium acetate after addition of tylose for suppressing maxima.

EXPERIMENTAL;RESULTS

Polarograms were registered as usual on a type V 301 Heyrovsky polarograph (Zborevka, Brno). The galvanometer which was a type Z9 had a maximum sensitivity of $3.5 \cdot 10^{-9}$ a/mm/m, an oscillation period of 9.5 seconds, an aperiodic resistance of 2000 Ω and an internal resistance of 152 Ω. A Kalousk cell with a saturated calomel electrode was used. Oscillographic observations were made by means of a P 524 polaroscope (Krzhizhik, Prague).

Nessler reagent was prepared as follows: 6 g of $HgCl_2$ was dissolved in 50 ml of warm water (80°) and a solution of 7.4 g of potassium iodide in 50 ml of water added to it. On cooling, the clear solution was poured off and the precipitate of HgI_2 washed three times by decantation with 20 ml lots of cold water for removal of chloride ions. 7.4 g of potassium iodide and a little water was then added; the solution obtained was poured into a 100 ml flask and 20 g of NaOH dissolved in a small amount of water added; on cooling, the whole was diluted with water to 100 ml. When the liquid had clarified, the clear solution was carefully decanted into a dark colored glass vessel.

The precipitates formed by the Nessler reagent dissolve readily in sodium thiosulfate. This solvent removes elemental iodine at the same time.

The solution of sodium thiosulfate to be used was studied polarographically first; subsequently, solutions in sodium thiosulfate of the precipitates formed with Nessler reagent were studied.

Polarographic Behavior of Sodium Thiosulfate

The depolarizing action of $S_2O_3^{2-}$ ions has already been observed by many authors, most of whom only mention one anodic wave. This wave, which, according to Kolthoff and Miller [19, 20], is most clearly defined in 0.1 M KNO_3 and has a half wave potential of 0.15 V (against the saturated calomel electrode) can be explained by formation of complex ions of $Hg(S_2O_3)_2^{2-}$ during anodic solution of mercury. The authors mentioned however, observed under these conditions at a potential of +0.15 V a second ill-defined wave which coincided with the "free wave" of the anodically dissolving mercury of +0.4 V. They explain this second wave at +0.15 by irreversible oxidation of thiosulfate to sulfite. We found that sodium thiosulfate exhibits a more complicated polarographic behavior, as Fig. 1 shows.

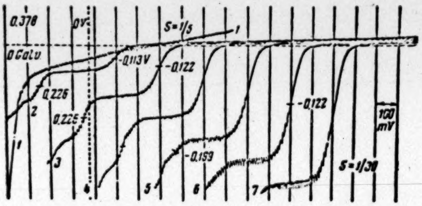

Fig. 1. Anodic Waves of Thiosulfate.
Curve 1) 4.5 ml of 1 M KNO_3, solution swept with nitrogen, polarographed anodically-cathodically from +0.378 (saturated calomel electrode); agar-agar bridge (3% agar-agar in 5% KNO_3). The curve was recorded at a sensitivity of 1/5 without compensation for the capacity current. Curve 2-7) to a solution similar to that in 1 was added gradually 0.01 ml at a time (0.06 ml altogether) of 0.1 M $Na_2S_2O_3$ and polarograms recorded at a sensitivity of 1/30. The curves are shifted through one chart width equivalent to 100 mv.

In a supporting electrolyte of 0.1 M KNO_3, at a thiosulfate concentration of about 10^{-4} M, two anodic curves can be observed on the polarogram at half-wave potentials of +0.22 and -0.12 V (Curves 2 and 3, Fig. 1). At thiosulfate concentrations of about 10^{-3} M, the more positive wave at + 0.22 V disappears and there appears a small indistinct wave at -0.19 V (Curve 5, Fig. 1), while the characteristic wave at the more negative potential preserves its half-wave potential constant, independently of the concentration. At concentrations greater than 10^{-3} M, only the characteristic wave at -0.12 V remains. Because the waves are so ill-defined, it is impossible, on the basis of the relationship between their heights and mercury flow rate, to conclude with any degree of assurance whether or not one of them is an adsorption wave. On carrying out an oscillographic study of low thiosulfate concentrations by means of dropping mercury electrode, it is possible to observe up to four cathodic peaks on the Shevchik curves. At high thiosulfate concentrations only one cathodic peak and an anodic peak, symmetrical with respect to the cathodic peak is observed. This simpler behavior is also observed with a streaming mercury electrode.

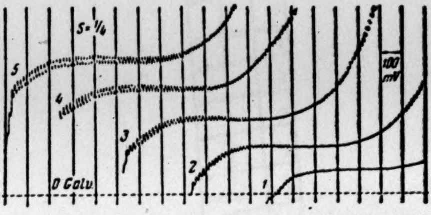

Fig. 2. Calibration polarograms for ammonia.
Solution A) 0.1 ml of aqueous 0.00025 M ammonia solution was precipitated with a few ml of Nessler reagent. The precipitate was collected on a G_5 filter and after washing with 0.1 N NaOH was dissolved in 10 ml of 25% sodium thiosulfate; Solution B) a 25% solution of $Na_2S_2O_3$. Curve 1) 9 ml of solution B was swept with nitrogen in a polarographic cell and polarograms taken cathodically from 0.3 V at a sensitivity of 1/4. Curves 2-5) to a solution as used in 1 was gradually added 1) 0.1 ml; 2) 0.12 ml; 3) 0.20 ml; 4) 0.20 ml of Solution A and polarograms taken under the same conditions. Kalousk cell with a saturated calomel electrode; capacity current partially compensated (in position 12).

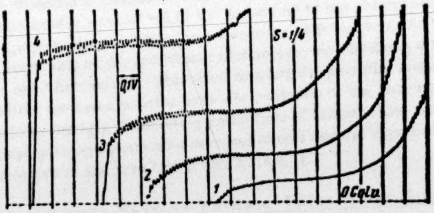

Fig. 3. Calibration curve for methylamine.
Solution A) 0.53 mg of methylamine hydrochloride was precipitated by addition of a few ml of Nessler reagent. The precipitate was collected on a G_5 filter and after washing with 0.1 N NaOH was dissolved in 5 ml of a 25% solution of thiosulfate. Solution B) 25% aqueous $Na_2S_2O_3 \cdot 3H_2O$ solution. Curve 1) 9 ml of solution B was swept with nitrogen in a polarographic cell, and polarograms taken from -0.3 V at sensitivity of 1/4. Curves 2-4) to a solution similar to that in 1 was gradually added 1) 0.2 ml; 2) 0.5 ml; 3) 1.0 ml of Solution A and polarograms taken under the same conditions. Kalousk cell with saturated calomel electrode; capacity current partially compensated (in position 12).

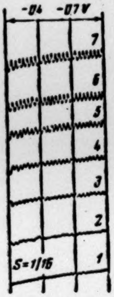

Fig. 4. Calibration polarogram for ammonium salts. Volumes 1) 0.2 ml; 2) 0.4 ml; 3) 0.6 ml; 4) 0.8; 5) 1.0 ml; 6) 1.2 ml $4.4 \cdot 10^{-3}$ solution of NH_4Cl were precipitated by addition of 3 ml of Nessler reagent. Precipitates were collected on a Gooch crucible packed with asbestos, and after washing with water were dissolved in 25 ml of a solution of 25% thiosulfate. Curve 1) 25% $Na_2S_2O_3$ solution swept with nitrogen in a polarographic cell and polarograms taken from 0.4 to 0.7 V at a sensitivity of 1/16. Curves 2-7) Solutions of the precipitates were polarographed under the same conditions.

These observations, as well as the ideas expressed by Kolthoff and Miller [19,20], testify to irreversible oxidation of thiosulfate to sulfite; the possibility of adsorption phenomena, or formation of various complexes between mercury which dissolves at the anode and thiosulfate, are not excluded. These complexes are most readily formed at low thiosulfate concentrations, since at higher thiosulfate concentrations a complex is formed which exhibits only one anodic wave at -0.12 V. According to our observations the corresponding depolarization process is oscillographically reversible (at a frequency of 50 cycles). At high thiosulfate concentrations—when the thiosulfate itself acts as the indifferent electrolyte—on dissolving a Millon base, there appears in the anode region only its one "free wave." This wave restricts the potential range at more positive values; nevertheless, it does not affect the more positive cathodic reduction of the mercury (in so far as we are dealing with a reversible process) from strongly dissociating complexes of Millon's base with thiosulfate. As a result of this the cathodic part of the polarographic curve does not have a normal exponential form and the limiting current is here only a shift relative to the zero line (Figs. 2,3,4,6,7).

Polarography of Millon's Base in Sodium Thiosulfate Solution

At high concentrations of ammonia and ammonium salts, a brown or dark brown precipitate is formed after addition of Nessler reagent, while primary, secondary, and tertiary amines, and quaternary bases give precipitates which are yellow or white-yellow in color but rapidly change in color (Table 1).

Every precipitate mentioned in Table 1 was collected on a filter and, after washing with 0.1 N NaOH, was dissolved in 25% (about 1 N) sodium thiosulfate. The transparent, colorless solution was polarographed in a nitrogen atmosphere; in all cases a current shift in the null galvanometer was only observed in the cathodic part.

From the calibration polarograms of ammonia, methylamine, and ammonium salts (Figs. 2,3 and 4) it is clear that if one assumes that quantitative precipitation by Nessler reagent occurs, and that the precipitates are washed free enough of reagent, it should be possible to use these reactions for analytical purposes.

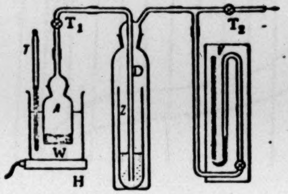

Fig. 5. Apparatus for vacuum distillation of volatile amines. A) vessel for sample; W) water bath; T) thermometer; H) hotplate; D) Dreschel bottle; Z) tube with Nessler reagent; V) Vacostat; T_1T_2 ground glass stop cocks.

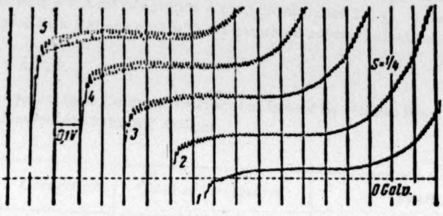

Fig. 6. Calibration polarogram for amines from meat. Solution A) 0.5 g of meat (beef which has been stored in a refrigerator at -5° for four days after killing and then at 26° for 4 hours in a thermostat) was ground up with sand and all the volatile amines distilled off under vacuum into Nessler reagent. The precipitate was collected on a G_5 filter and after washing with 0.1 N NaOH was dissolved in a 25% solution of $Na_2S_2O_3 \cdot 3H_2O$; Solution B) 25% aqueous solution of $Na_2S_2O_3$ $3H_2O$; Solu-C: 10% solution of $Na_2SO_3 \cdot 3H_2O$; Curve 1) 4.5 ml of solution B and 4.5 ml of solution C were mixed in the polarographic vessel and polarograms taken in the presence of air cathodically from 0 V at a sensitivity of 1/4. Curves 2-5) to the solution which gives Curve 1 was gradually added 0.5 ml of solution A and polarographed under the same conditions. Kalousk cell with a saturated calomel electrode; capacity current partially compensated (Position 15).

By using a small pore bacteriological filter G_5, it is possible to filter small amounts of very fine grain, almost colloidal precipitates, and thus achieve fairly high sensitivity. Strongly alkaline solutions of Nessler reagent, however, dissolve the porous filter discs which accordingly become more permeable and rapidly become unsuitable for further filtration. We succeeded in filtering very fine precipitates by using asbestos on a Gooch crucible, and obtained a satisfactory linear relation between current and concentration (Fig. 4).

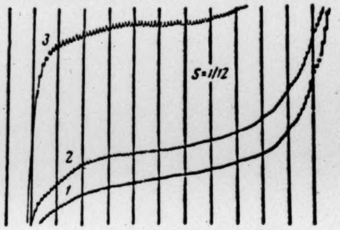

Fig. 7. Degree of necrosis of rat tumor.
Solution A) an aliquot of rat tumor Walker 256 was ground up with sand immediately after sacrifice and all the volatile amines distilled off under vacuum into Nessler solution. The precipitate was collected on a G_5 filter and washed with 0.1 N NaOH and dissolved in 4.5 ml of 25% $Na_2S_2O_3 \cdot 3H_2O$; Solution B) 25% solution of $Na_2S_2O_3 \cdot 3H_2O$. Curve 1) solution B was swept with nitrogen and polarographed cathodically at a sensitivity of 1/12. Curve 2) 4.5 ml of solution B + 0.5 ml solution A (aliquot of rat tumor 0.5 g). Curve 3) 4.5 ml of solution B + 0.5 ml of solution A (weight of tumor 2.5 g). Solutions were polarographed in a Kalousk cell with the saturated calomel electrode.

TABLE 1

Approximate Colors of Precipitates formed by Nessler Reagent with Ammonium Salts and Amines

Compounds	Color of precipitate	Notes
NH_4 salts	Dark brown	—
NH_3, NH_4Cl	Brown	—
CH_3NH_2	White	On addition of alkali the color changes to yellow
$(C_2H_5)_3$ N	Dirty yellow	At high concentrations the color is ochre
$(CH_3)_4$ NOH	Yellow, sulfur color	Whitens rapidly
$(CH_3)_4$ NI	Yellow	Whitens rapidly

A calibration curve for ammonium salts was constructed as follows: to 3 ml lots of Nessler reagent was added successively, by means of a micro-pipet, from 0.05 to 0.60 ml of an aqueous solution of $4.4 \cdot 10^{-3}$ M NH_4Cl; the precipitate was collected on a G_5 filter and after washing with 0.1 NaOH was dissolved in 2.5 ml of 25% sodium thiosulfate. 0.5 ml of this solution was pipetted into a Kalousk cell containing 4.5 ml of 25% sodium thiosulfate. A linear relation between current and concentration was established when polarograms were taken in a nitrogen atmosphere. Atmospheric oxygen can also be removed by addition of sodium sulfite.

Quantitative distillation of volatile amines and ammonia from various products, such as meat samples, or pickling brines was carried out in the apparatus shown in Fig. 5.

Test sample is introduced into flask A (about 0.5 g is sufficient when analyzing meat, and about 0.5 ml when analyzing brine); the meat is ground up with sand in order to increase its surface area. The sample is heated in bath B (which is in turn heated by the hot plate D) to 40-50°, while at the same time the scrubber P is evacuated. After 30-60 minutes the sample of meat is dried (the brine is evaporated) and all volatile amines and ammonia are precipitated in tube Z in which Nessler reagent solution acts as air lock. Polarographic determinations are then carried out as described already. By comparing the heights of the polarographic wave for test meat and meat which is known to be fresh, it is possible to estimate the extent of putrefaction of the test meat (using the same type of meat and using equal weights) on the basis of total amine content.

As an example of the application of the method we have developed to medicine we quote the evaluation of the degree of necrosis of a cancerous tumor in a rat (Fig. 7). This was in connection with the six weeks transplantation of Walker 256 tumor (the state at which the rat may expect to live another 2 weeks at the outside). The experiment was carried out immediately after sacrifice of the animal, the sample being taken from a strongly necrotic part of the tissue. The amount of volatile amine materials was found to be considerably greater than in the tissue of a healthy rat.*

The authors wish to thank Dr. Gratz of the Oncological Institute of Bulovka in Prague for his gift of biological material.

SUMMARY

A method has been developed for determination of ammonia and amines; it is based on their precipitation with Nessler reagent, and subsequent polarographic determination of mercury in the precipitate obtained after conversion into the thiosulfate complex.

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* The maximum temperature of the water bath B during vacuum distillation should not be higher than 40-50°. Distillation of volatile amine-like materials should not be similar in character to steam distillation. In the latter event, there would be continuous liberation of volatile amine-like materials from protein prosthetic groups as a result of hydrolytic break down of the proteins.

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A SEMIMICRO METHOD FOR THE DETERMINATION OF CELLULOSE AND PENTOSANS IN WOOD

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The macro methods most frequently used at present for the quantitative determination of cellulose and pentosans in wood require a large amount of test material (1-2 g). Such are the methods of Cross-Bevan, Kurshner, and some others for cellulose, and the classical method of Tollens for pentosans. Frequently, however, the analyst only has a small amount of test material at his disposal; this sometimes either makes it impossible to carry out a quantitative determination of pure cellulose, free from pentosans, or makes such a determination difficult. It has been apparent for some time therefore that there was a need to develop a semimicro method for determining the main components of wood cell walls.

There is a fairly satisfactory semimicro method for the determination of lignin [1], which we have ourselves used successfully; nevertheless, the suggestion put forward by Runger and Klauditz [2] in 1953 for determination of cellulose and pentosans by a semimicro method proved—as we showed experimentally—not completely satisfactory, since it is necessary to transfer the exceedingly small amount of cellulose involved from one apparatus to another in order to determine the residual hemicellulose; such an operation is inevitably accompanied by loss of material. Further, when their technique is used, during the determination of pentosans, the distillate containing furfural is collected in an open measuring cylinder; this leads to loss of furfural which cannot be tolerated in a semimicro method.

We developed in 1951 a more suitable technique for determining cellulose and pentosans in one aliquot. The basis of our technique is the nitric method [3] of determining cellulose, with subsequent determination in the same aliquot of pentosans by hydrolysis with 13% hydrochloric acid [4]. All the analysis is carried out in one reaction vessel.

Apparatus. The apparatus (Fig. 1) for determining cellulose consists of a 50 ml round bottom flask 1 with ground glass neck, a filter stick 2, a spherical shaped inner tube condenser 3 which is 18 cm long, and a stopper of the shape shown 4.

The apparatus for determining pentosans (Fig. 2) consists of: a 50 ml flask with the same size ground glass neck as that for cellulose determination; a small fractionating column 2 of the shape shown for preventing foam from getting into the receiver; a calibrated 15 ml dropping funnel which is connected to the fractionating column through a ground glass joint; a spherical condenser 4 which is 12 cm long; and a 100 ml calibrated receiver 5 with the appropriate ground glass joint for connecting it to the condenser—this receiver used for collecting the distillate is provided with a fused in water seal 6.

Determination of Cellulose. Before analysis, flask filter stick half filled with asbestos, and the stopper are first of all washed with chromic acid by sucking the latter a few times through the filter stick, the cleaning operations are repeated with distilled water. 10 ml of exactly the same mixture of 8 ml of ethanol and 2 ml concentrated nitric acid as that used for an analysis is then poured into the flask into which the filter stick has been inserted. The flask is connected to the reflux condenser and the mixture heated to boiling with the nitric-alcohol mixture for 15 minutes; the mixture is then sucked off and the apparatus washed with pure ehtanol by drawing it through the filter stick; the apparatus is finally dried at 105° over P_2O_5 to constant weight. During weighing and also for other further manipulations the reaction flask is only handled with a piece of chamois.

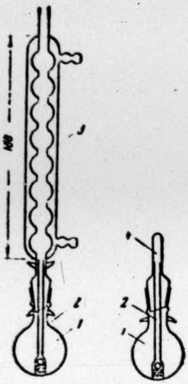

Fig. 1.

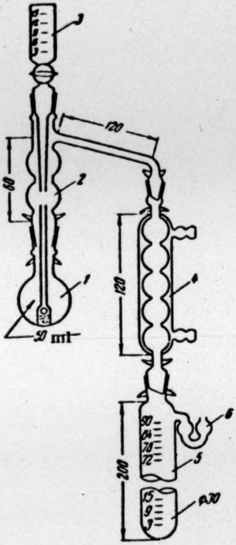

Fig. 2.

0.1 g of absolutely dry test material is weighed into a flask prepared in this way, the filter stick is inserted, and 10 ml of a mixture of 8 ml ethanol and 2 ml concentrated nitric acid added. The flask is connected to the reflux condenser and heated on an air bath at 90° for one hour. After this period liquid is carefully filtered free of the precipitate through the filter stick. Boiling with the nitric-alcohol mixture is repeated twice again. The residue of crude cellulose thus obtained is washed with the mixture of ethanol and nitric acid and then boiled for another 30 minutes with 20 ml of distilled water. The liquid is sucked off and the residue washed with distilled water until the washings give a neutral reaction, the washings being sucked off each time; the residue is dried in the reaction flask with filter stick and stopper at 105° in a vacuum over P_2O_5 to constant weight. The weight of crude cellulose – i.e., cellulose plus a small amount of sparingly soluble hemicellulose – is thus obtained.

Determination of Pentosans. The amount of pentosans in the crude cellulose obtained as described above is determined in the same reaction flask (plus filter stick). The cellulose and asbestos lodged in the filter stick are pushed out by means of a fine glass rod into the flask and the filter stick stoppered with a small lump of asbestos to prevent liquid rising in it during boiling.

5 g of sodium chloride is introduced into the flask which is then connected to the fractionating column, condenser and receiver; a few drops of 13% hydrochloric acid is introduced into the water seal of the receiver. When the apparatus has been assembled, 10 ml of 13% hydrochloric acid is introduced into the reaction flask by means of the dropping funnel. Heating is carried out on an air bath so that the distillate comes over at the rate of 1 ml/minute. After distillation of each 3 ml, another 3 ml of 13% hydrochloric acid is introduced from the funnel to replace it. 90 ml of distillate is collected altogether. The distillate is transferred to a 100 ml standard flask and its volume made up to the mark with 13% hydrochloric acid.

The furfural content of the distillate is determined by means of the bromide-bromate method. Into a ground glass necked flask is introduced 25 ml distillate and 75 ml of distilled water added; this is followed by 2 ml of ammonium molybdate solution (25 g in 1 liter water) and 5 ml of 0.05 N bromide-bromate (10 g KBr; 1.392 g $KBrO_3$ in 1 liter water). The flask is stoppered immediately and allowed to stand for 4 minutes in diffuse light. 5 ml of 10% potassium iodide solution is then added to the reaction mixture. The flask is stoppered again and after another 5 minutes titrated with 0.05 N sodium thiosulfate. A blank is carried out in exactly the same way.

The method has been checked by comparing the results obtained by this technique and by a macro method when the same samples were analyzed (Table).

TABLE

Determination of Cellulose and Pentosans by Macro- and a Semimicro Methods

Test material	Cellulose as a % of the absolutely dry, ashless material		% Pentosans in the cellulose		% Pentosans in the absolutely dry, ashless material	
	Macro method	Semimicro method	Macro method	Semimicro method	Macro method	Semimicro method
Birch	42.98 43.08	42.72 42.77	6.63 6.58	6.65 6.62	24.28 24.36	24.35 24.31
Spruce	51.49 51.40	51.31 51.27	5.75 5.82	5.81 5.83	12.43 12.36	12.43 12.40

Macro-analysis was carried out by means of the Kurshner method; an aliquot of the cellulose obtained was then introduced into a Jeime-Sarten apparatus and the amount of pentosans was determined by the Tollens method. Pentosans were determined by the semimicro method using the technique described above. Further pentosans were determined independently in wood both by the macro method and by the semimicro method; the apparatus was also checked on pure xylose.

The following results were obtained when the apparatus was checked by means of pure xylose: xylose taken 0.0324 g, 0.0295 g; xylose found 0.0317 and 0.0287 g.

SUMMARY

1. Kurshner's method for the quantitative determination of cellulose, and the Tollens reaction for determination of pentosans, have been modified so that they can be used on a semimicro scale.

2. The method proposed is very suitable for determination of cellulose and pentosans on one aliquot of sample, and can be carried out in the same reaction flask.

3. The semimicro method of determining cellulose and pentosans gives reproducible results which are in good agreement with those of macro analysis.

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QUANTITATIVE DETERMINATION OF STREPTOMYCIN AND MANNOSIDOSTREPTOMYCIN IN FERMENTATION BROTHS AND IN INTERMEDIATE PRODUCTS OF STREPTOMYCIN PRODUCTION

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During biosynthesis of streptomycin a fermentation broth is obtained, which, in addition to streptomycin, contains various organic and inorganic materials-products of the activity of the micro-organism (Actinomyces globisporus streptomycini), residues of the nutrient medium, and mycelium. In some cases, not only streptomycin (SA) is formed during biosynthesis, but another biologically active material which is very similar in chemical and physical properties to SA, and differs from SA only in that it contains a d-mannose residue in the molecule: this substance is mannosidostreptomycin (MS). The antibiotic activity of MS is considerably lower than that of SA, while both materials are similar with respect to toxicity. Naturally, the presence of MS in fermentation broths of streptomycin is undesirable. Accordingly in order to follow the dynamics of the accumulation of SA and MS, and follow the enzymatic conversion of MS into SA it is necessary to determine the concentrations of SA and MS during biosynthesis.

In order to determine SA and MS chemically in fermentation broths, it is first of all necessary to separate them quantitatively from impurities which interfere with the photometric determination of these antibiotics.

Their ready sorption by cation-exchange materials was used for separating MS and SA from these impurities. This technique was used by John et al., [1] for determination of MS in fermentation broths. The cation-exchanger they used was Amberlite IRC-50.

The effect of diluting the solution was used by us in the technique we have developed for separating SA and MS and impurities. On diluting the solution more favorable conditions are created for extracting the polyvalent ions of SA and MS from solution by the cation-exchange resin [2]. By diluting the native solution,* we were able to carry out quantitative sorption of the streptomycins with silica gel. Silica gel under these conditions acts as a weakly acid cation-exchanger [3]. Subsequently, SA and MS were completely eluted from silica gel by means of acid, and SA and MS determined in the purified eluate photometrically.

Numerous experiments carried out with samples of fermentation broth taken at various stages of the biosynthesis showed that under the conditions we selected, streptomycin is completely extracted by silica gel. completeness of sorption was checked by means of the most sensitive micro-biological method of determining streptomycin. Silica gel has the very valuable property of yielding up all the streptomycin which it has sorbed when it is subsequently eluted with acid. This was demonstrated by sorbing a known amount of the streptomycins and recovering the same amount in the eluate, and also by addition of streptomycin to a fermentation broth and determining it in the eluate obtained after desorption from silica gel.

In this way we developed a technique for quantitatively separating streptomycin from native solution by means of silica gel followed by complete elution of SA and MS with acid. The eluate obtained does not contain impurities which interfere with determination of the streptomycins.

A confirmation of the fact that we are actually determining the true concentration of SA and MS when our method is used is the coincidence between the microbiological activity calculated on the basis of the concentrations of SA and MS, and the activity as determined by diffusion of the antibiotic into agar (the method normally used).

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* Native solution – the fermentation broth from which mycelium has been separated.

1. Removal of Mycelium from the Fermentation Broth. Finely ground oxalic acid (r) is added to the fermentation broth with vigorous agitation until pH is about 2. After 15 minutes the liquid is filtered or centrifuged to give the native solution.

2. Preparation of the Silica gel. Silica gel Mark ASK (Voskresensk Chemical Combine) is sieved and the fraction with particles 0.25-0.5 mm collected; this fraction is washed with tap water; concentrated nitric acid is then added and the whole heated for 20 minutes on a boiling water bath. After decanting the acid, the silica gel is washed with soft water to a neutral reaction to methyl orange.

In order to convert it into the sodium form, the silica gel is covered with a saturated solution of sodium carbonate and left to stand for 2-3 hours, after which it is washed with distilled water for removal of excess sodium carbonate; it is stored under water.

3. Sorption of SA and MS by Silica gel and Washing of the Latter. An amount of native solution is taken such that on dilution to a liter the concentration of streptomycin is about 10γ/ml. The pH is adjusted to 8.3-8.5 (phenolphthalein) by means of 10% sodium hydroxide. 16 cm^3 of silica gel in the sodium form (measured out with a measuring cylinder) is taken and added with a small amount of water to the diluted streptomycin solution. Solution + silica gel are shaken for 1 hour, after which the solution is decanted and the silica gel washed with two lots of 150 ml of water; the silica gel is then transferred to a glass column ($d = 18$ mm; h about 150 mm) which is fitted at the bottom with a porous glass disc ("Druzhnaya gorka" No. 1). The silica gel is washed with 100 ml of water in the course of 30 minutes. The silica gel should be transferred quantitatively into the column; otherwise some of the streptomycin sorbed by it will be lost to analysis.

4. Elution of SA and MS. On completion of washing, water is left in the column with its level not more than 3-5 mm higher than the silica gel level. Elution is carried out with 1 N sulfuric acid at the rate of 100 ml/hour, the eluate being collected in a 50 ml flask. In order to maintain the required elution rate it is convenient to use a capillary chosen beforehand and fitted by means of a rubber tubing to the "tail" of the column.

5. Determination of SA and MS in the Eluate. 20 ml of eluate is transferred to a 25 ml standard flask. 1-2 drops of phenolphthalein is added and 20% sodium hydroxide then added until the solution has a weak rose color. The solution in the flask is made up to the mark with distilled water. The concentrations of SA and MS are determined in the solution obtained by the maltol method [4].

6. Determination of MS in the Eluate. MS concentration is determined directly in the acid eluate by the anthrone method [5].

From the concentrations obtained, the concentration of SA and MS in the original native solution is then calculated.

We carried out a series of tests with various fermentation broths, calculating the microbiological activity from the results of chemical determinations, and also determining the activity directly in the Biocontrol Laboratory of the All-Union Scientific Research Institute of Antibiotics. Not less than 12 activity determinations were made on each sample.

It is usual to express microbiological activity in terms of microbiological units where 1000 γ SA (as the base) corresponds to 1000 microbiological units, while 1000 γ MS is equal to 240 microbiological units. Then the microbiological activity calculated from the concentrations of SA and MS is equal to $(581\, a_{SA} + 0.24 \cdot 743 \cdot a_{MS})\, 10^3$ where a_{SA} is the concentration of SA in millimols ml; a_{MS} is the concentration of MS in millimols/ml; 581 is the molecular weight of the SA base; and 743 is the molecular weight of the MS base.

Using this method we calculated the microbiological activity of a number of samples. If we take the microbiological activity as determined by diffusion in agar as 100%, then for individual samples the calculated activity amounted to 100, 95, 102, 100, 103, 101, 93%. Such agreement is completely satisfactory and confirms the correctness of our method for determining the concentration of SA and MS in native solution. The method can be used for determining SA and MS at all stages of chemical purification.

We should like to thank L. S. Buyanovska for regular help in the microbiological work.

SUMMARY

A method has been developed for the chemical determination of streptomycin (SA) and mannosidostreptomycin (MS) in fermentation broths.

SA and MS are separated from impurities in solution by ion-exchange using silica gel in the sodium form. SA and MS are quantitatively removed from diluted fermentation broths by silica gel. The antibiotics are subsequently eluted from silica gel by means of sulfuric acid. After elution, SA and MS are determined by the maltol (SA + MS) and anthrone (MS) methods.

The microbiological activity of a sample can be calculated on the basis of the concentrations of SA and MS found by this method. The values obtained in this way are in good agreement with activity determined directly by the normal method of microbiological assay.

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* (U.S.S.R.)

** See C. B. Translation.

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CARRYING OUT ORGANIC SEMIMICRO ANALYSIS IN MACRO ANALYTICAL APPARATUS

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Micro elemental analysis takes less time to carry out and requires less test material than macro analysis; in consequence it is displacing the latter.

At the moment there are two basic methods of organic micro analysis which differ in principle from each other. The first of these, which was developed by Pregl [1], is a micro modification of the classical Liebig method. Subsequently Friedrich [2], J. Niederl and V. Niederl [3], as well as some other authors have modified Pregl's original technique. In this method analysis is carried out in combustion tubes in the presence of so call "universal" or "combined" filler. Decomposition of test material is carried out in a weak current of oxygen under a positive pressure at temperatures of 750-800°.

The second method of micro analysis has been developed in the course of recent years by Korshun [4-6]. In this case, analysis is carried out in an empty tube in the absence of any filler or catalytic contacts. The test material is subjected to pyrolytic decomposition in almost complete absence of oxygen while the pyrolytic products are ignited without increasing the pressure in a rapid stream of oxygen at 850-900°. This method is simple, rational, and accurate. By using Korshun's technique, the analyst is freed from a lot of tedious work connected with the use of filler, regulators for pressure, etc., and the other apparatus used in the classical methods of micro analysis.

At present, most laboratories carrying out organic analytical work are equipped with macroanalytical apparatus. In view of the difficulty with regard to supplies of microanalytical apparatus and weights, we thought it would be expedient to adapt macroanalytical apparatus for carrying out semimicro elemental analysis. In order to adapt macroapparatus for the rapid method the following changes were made: no filler was used in the quartz combustion tube, the platinum boat which contains the test aliquot was replaced by a quartz vessel 88 mm long and 8 mm in diameter, while the absorption apparatus for carbon didoxide and water were replaced by open Pregl absorption tubes* containing askarite and anhydrone. The shorter of the two electric furnaces used with the macroapparatus was replaced by a burner.

An aliquot of test material (30-50 mg) was weighed out on a normal analytical balance with an accuracy of up to 0.1 mg. The analytical procedure was the same as for the rapid micromethod; oxygen supplied from a cylinder and purified as usual was passed into the combustion tube and flowed round the tube containing the sample.

Pyrolysis of test material was effected by heating it with the burner to 950° in excess oxygen at an optimum oxygen throughput of 38-45 ml/minute.

The combustion products of the pyrolytic gases were sucked by an aspirator through the absorption apparatus. Depending on the composition and structure of test material, pyrolysis, complete combustion, and exhaust from the tube of the combustion products took from 25 to 40 minutes. The deviations of the results actually obtained with this technique from theory were within permissible limits.

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* 140 mm long and 10 mm in diameter with capillary constrictions 25 mm long at the ends.

TABLE 1

Material	Analytical method	Weight sample taken, g	Carbon, in %			Hydrogen, in %		
			found	calcu-lated	differ-ence	found	calcu-lated	differ-ence
Di-(α-methyl-α-hydroxyethyl)-cyclooctatriene, b.p. 144-153° (3/5 mm) $C_{14}H_{22}O_2$	Macro	0.0916	75.48	75.68	—0.2	10.12	9.91	+0.21
	Semimicro	0.0524	75.67	—	−0.01	10.0	—	+0.09
Benzoic acid $C_7H_6O_2$, b.p. 121°	Macro	0.1008	68.61	68.85	—0.24	5.11	4.92	+0.19
	Semimicro	0.0382	68.86	—	+0.01	5.03	—	+0.11
3-Hydroxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene $C_{14}H_{13}O$, b.p. 151-152° (3 mm)	Macro	0.0783	83.24	83.16	+0.08	9.09	8.91	+0.18
	Semimicro	0.0467	83.33	—	+0.17	8.97	—	+0.06
Di-(α-methyl-α-hydroxypropyl)cyclooctatriene $C_{16}H_{22}O_2$, b.p. 158-167° (3 mm)	Macro	0.1046	77.15	76.80	+0.35	10.48	10.40	+0.08
	Semimicro	0.0471	76.89	—	+0.09	10.47	—	+0.07
Diacetate of 2-methyl-3-hexanonedione-2,5 $C_{11}H_{13}O_5$, b.p. 102-103° (2 mm)	Macro	0.0993	57.04	57.39	+0.35	7.93	7.82	+0.11
	Semimicro	0.0472	57.37	—	+0.02	8.05	—	+0.23

TABLE 2

Material	Weight sample taken, g	Carbon, in %			Hydrogen, in %		
		found	calcula-ted	differ-ence	found	calcu-lated	differ-ence
Di-(α-phenyl-α-hydroxyethyl)cyclooctatriene $C_{24}H_{26}O_2$, b.p. 280-238° (3 mm)	0.0454	83.50	83.24	+0.26	7.82	7.51	+0.31
	0.0494	83.47	—	+0.23	7.77	—	+0.26
Benzoic acid $C_7H_6O_2$, b.p. 121°	0.0330	69.09	68.85	+0.24	5.21	4.92	+0.29
	0.0378	69.14	—	+0.29	5.11	—	+0.19
	0.0398	68.86	—	+0.01	5.13	—	+0.21
2-Methyl-4-carboxyphenoxyacetic acid $C_{12}H_{16}O_5$, b.p. 279-280°	0.0326	56.97	57.14	−0.17	5.11	4.76	+0.35
	0.0480	57.05	—	—0.09	5.00	—	+0.24
α-(Butyl) capronic acid $C_{10}H_{18}O_2$, b.p. 109-110° (1 mm)	0.0450	71.15	71.42	−0.27	9.63	9.52	+0.11
Di-(α-ethyl-α-hydroxypropyl) cyclooctatriene $C_{18}H_{30}O_2$, b.p. 174-182° (3 mm)	0.0443	77.93	77.70	+0.23	10.83	10.79	+0.04
	0.0430	77.88	—	+0.18	11.06	—	+0.27
3-Keto-1,2,3,4,4a,9,10,10a-octahydrophenanthrene $C_{14}H_{16}O$, b.p. 165-167° (3 mm)	0.0506	83.81	83.94	−0.13	8.19	8.06	+0.13
	0.0452	83.68	—	−0.26	8.17	—	+0.11

Table 1 contains a comparison of results obtained by the normal macroanalytical method and by the rapid semimicro method described above.

As these results show, the method which has been developed is more accurate and can be carried out more rapidly than the macro method.

Table 2 contains some results obtained by means of the semimicro method described for some other materials belonging to various classes of organic compounds.

SUMMARY

It has been demonstrated that it is possible to carry out quantitative carbon and hydrogen determinations on a semimicro scale by means of a macroanalytical apparatus using the rapid micro method of M. O. Korshun.

The semimicro technique developed gives more accurate results and is carried out more rapidly than the macro method.

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BRIEF COMMUNICATIONS

THE ANALYTICAL APPLICATION OF SOME DYES CONTAINING OH-GROUPS

PART 1. NEW HIGHLY-SENSITIVE SELECTIVE REACTIONS FOR ANTIMONY

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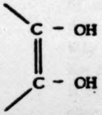
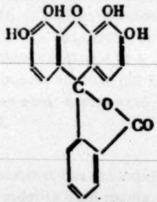
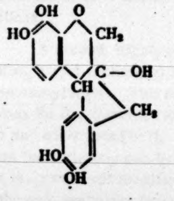
The presence of two enol hydroxyls in the ortho position with respect to one another determines the interreaction of organic reagents with trivalent antimony. The group of atoms



in the aromatic nucleus [1] is assumed to be a functional analytical group (specific) for trivalent antimony. During a study of the behavior of gallein (I) (3',4', 5', 6'-tetrahydroxyfluorane) with other ions, we established that this reagent can be applied for detecting antimony trichloride by a trituration method [2]. In this case gallein, like other phthaleins [3], apparently forms a halochrome compound of a blue-violet or lilac color depending on the relative amounts of reagent and antimony trichloride.



(I)



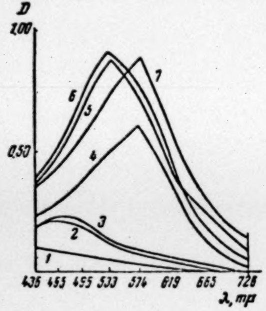
(II)

Of considerable practical interest is the use of gallein in a spot test for antimony and photometric determination of gallein by means of the same reagent. Under various conditions, as is evident from published data [4,8], and from our own experiments, gallein reacts with many cations. All the same, in 0.5 N HCl the color formed by gallein with the overwhelming majority of the cations we tested, apart from Sb^{III}, Sn^{2+}, and Sn^{IV}, is destroyed. The nature of the color of the compound formed between gallein and Sn^{2+} and Sn^{IV} is very similar to the color of gallein in acid media. In neutral aqueous solution, gallein on its own has a weak rose color; in acid media, the color is a rose-red; in strongly acid media the color is yellow; in alkaline media – rose-violet; very alkaline media – violet, changing to yellow with time. The reagent accordingly possesses indicator properties.

As our tests showed, gallein, under certain conditions, is a highly sensitive selective reagent for trivalent antimony. Quinquevalent antimony does not give a characteristic color.

The spot technique for Sb^{III} using gallein as reagent is carried out as follows. A drop of a 2% solution of gallein in acetone is placed on a filter paper; after drying (rose color) a drop of solution to be tested for Sb^{III} is placed on the same spot on the paper, followed by a drop of 0.5 N HCl (1 ml of the test solution is mixed beforehand with 1 ml of acetone). In the presence of antimony, a violet or rose-violet (depending on the amount of Sb^{III}) color on an orange background appears. The limit of identification – in the absence of other cations – is 0.005 γ, limiting dilution $1:3.3 \cdot 10^5$; in the presence of other ions the sensitivity drops to 0.05 γ.

Alkali and alkaline earth elements as well as Mg, Zn, Cd, Hg^{I}, Hg^{II}, Pb, Al, Fe, Cr^{III}, Co, Ni, Mn^{2+}, Cu, UO_2^{2+}, Th, Bi in amounts which are 1000–10,000 times that of the antimony, do not interfere; while Sn^{2+} and Sn^{IV} in amounts which are not more than 100 times that of the amount of antimony present, do not interfere.



1) Gallein solution (about 10^{-4} mol/liter); 2) solution of gallein + Pb^{2+} + CH_3COOH (5 mg/ml Pb^{2+}); 3) gallein solution + CH_3COOH; 4) gallein solution + Pb^{2+}; 5) gallein solution + Sb^{III} + CH_3COOH; 6) gallein solution + Sb^{III}; 7) gallein solution + Bi + CH_3COOH. In all cases an aqueous acetone (50% acetone) solution of gallein was used; acetic acid concentration was about 0.5 N.

We also established that it is possible to carry out a quantitative photometric determination of Sb and Bi and some other cations by means of gallein. On the diagram are given as examples absorption curves for a solution of gallein and for solutions of the corresponding compounds formed between gallein and the ions Sb^{III}, Bi, and Pb respectively. From these curves it is evident that antimony and bismuth can be determined separately in acetic acid media in the presence of lead (in the case of antimony the permissible amount of lead is determined by the solubility product of $PbCl_2$; in the case of bismuth, the amount of $Pb(NO_3)_2$ can exceed the amount of $Bi(NO_3)_2$ a thousand times). Many other cations do not interfere with the photometric determinations of Sb and Bi.

More detailed spectrophotometric characteristics of gallein, a description of its behavior towards various cations, as well as a method for the colorimetric determination of Sb^{III} and Bi will be included in a subsequent article.

A second, highly-sensitive reaction for antimony (using a spot technique) is the reaction of the latter with hematoxylin (II). This reagent has been used several times for the photometric determination of Al, Cr, Mo, Sn and other ions [5-7]. A fairly selective spot reaction for antimony can be achieved with hematoxylin. It should be pointed out, however, that this selectivity of the reagent is not manifested in solution because the reagent itself has a bright red color in acid media. Using the spot technique, however, hematoxylin can be used as a highly selective reagent for antimony in the presence of 0.5 N HCl. Antimony is detected by means of this reagent as follows: a drop of an acetone solution of hematoxylin (acetone saturated with hematoxylin at room temperature) is placed on a filter paper; a drop of the solution to be tested for Sb^{III} – mixed beforehand with an equal volume of acetone – is then placed on the same spot on the filter paper; after drying, the spot is moistened with 1-2 drops of 0.5 N HCl. If Sb^{III} is present, a blue or violet color on a red background appears. The limit of identification is 0.03 γ; the limiting dilution is $1:5 \cdot 10^4$. Other cations behave in the same way as they do in the reaction with gallein.

SUMMARY

Two selective and highly-sensitive spot reactions have been developed for Sb^{III} (with gallein and hematoxylin).

It has been demonstrated that it is possible to determine Sb^{III} and Bi photometrically by means of 3', 4', 5', 6'-tetrahydroxyfluorane (gallein).

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DETECTION OF ALUMINUM

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Detection and identification of aluminum is based on interaction of aluminum hydroxide with the fluorides of the alkali metals to form OH^- ions which are detected by means of phenolphthalein.

$$Al(OH)_3 + 6F^- \rightleftharpoons [AlF_6]^{3-} + 3OH^-.$$

A method for the quantitative determination of aluminum has been developed previously on the basis of this reaction [1]. To 1-2 drops of the test solution of an aluminum salt is added 1-0.01 N NaOH until the bright red color of phenolphthalein develops; 0.1-0.01 N HCl is then added dropwise until the solution becomes colorless, after which a few drops of about 1 N KF solution is added and the color of the solution observed. On the basis of the intensity of the rose color formed an estimate can be made of the amount of aluminum in solution. A more accurate idea can be gained by measuring the amount of acid which must be added to make the solution colorless again.

During detection of small amounts of aluminum when a more accurate neutralization of test solution must be carried out, removal of excess alkali is effected by means of atmospheric CO_2, the solution being shaken in a tube until the color disappears.

The limiting dilution during detection of aluminum is roughly 1: 1,100,000, while the limit of identification is about 1γ/ml. On ageing the reactive capacity of the aluminum hydroxide with respect to fluoride ions decreases appreciably [2].

The hydroxides of chromium, nickel, cobalt and ferric iron (3-4 drops of 0.5 N solutions of these salts were used for these tests; the final volume was 4-5 ml) do not liberate alkali even in the presence of excess potassium fluoride (up to 12 drops of 1 N potassium fluoride was added) and the solutions above the precipitates remain colorless. Manganese hydroxide under the same conditions does not liberate appreciable amounts of alkali either. The color of the hydroxide of quadrivalent manganese interferes, however. Zinc hydroxide precipitated from 3 drops of 1 N zinc sulfate gave a hardly perceptible amount of OH ions under the influence of 12 drops of 1 N potassium fluoride.

In the presence of other cations of the third analytical group, the solution being tested for aluminum is treated with excess NH_4OH in the presence of NH_4Cl, and the precipitates washed with water until the washings give a negative test for OH (test with phenolphthalein). The washed precipitate is suspended in 2-3 ml of water and treated with a few drops of 1 N potassium fluoride and 1-2 drops of phenolphthalein; it is washed, and, if necessary, centrifuged. If sufficient aluminum is present the solution above the precipitate of the hydroxides will be colored.

This method permits detection of as little as 3γ of Al^{3+} in a solution containing 300 times its amount of chromium, nickel, cobalt, zinc, manganese, ferric iron (in equivalents).

On separating aluminum by the peroxide and ammonia methods [3] from 150 times its amount Cr^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, and Fe^{3+} the limit of identification is about 5γ Al.

Solutions containing group II cations may sometimes be contaminated by silicic acid which may be precipitated with the aluminum hydroxide. Freshly precipitated and washed silicic acid, however, does not react with potassium fluoride to give a change in acidity. In the course of 10 minutes after treating an aqueous suspension of silicic acid with 1 N potassium fluoride, the pink color of phenolphthalein did not appear.

SUMMARY

Detection and identification of aluminum is based on interaction of aluminum hydroxide and fluorides of the alkali elements to form OH ions which are detected by means of phenolphthalein.

The limiting dilution is 1 in 1,100,000 while the limit of identification is about 1γ/ml. Silicic acid does not interfere.

A method for the detection of aluminum in a solution containing Cr, Mn, Zn, Co, Ni and Fe is described.

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A MIXED COLOR INDICATOR FOR THE DETECTION OF ETHYLENE OXIDE

V. A. Pokrovsky

A 35% aqueous solution of urotropine [1] or a saturated aqueous solution of thiosulfate [2] can be used for the detection of ethylene oxide. To 2-3 ml of one of these solutions is added 1-2 drops of a 1% alcohol solution of phenolphthalein. When air containing ethylene oxide is passed through such a solution, a rose color develops. Kolthoff indicator can be used instead of phenolphthalein (the former is made of equal volumes of aqueous solutions of 0.1% Methyl Orange and 0.25% Indigo Carmine.

Clearly defined colors and sharp transitions are observed on using a mixed indicator consisting of aqueous solutions of Indigo Carmine, Cresol Red, and Methyl Orange. During the detection of ethylene oxide by means of urotropine, this indicator changes color from red-green to blue, while with thiosulfate the color change is from light green to violet. The color change—particularly with thiosulfate—is exceptionally sharp and can be readily observed both by daylight and by artificial light. This indicator gives a similar sharp and readily observable change in color during titration of dilute solutions from acid to alkali and vice-versa.

The sensitivity of the qualitative reaction for ethylene oxide in 35% solutions of urotropine and thiosulfate with the new mixed indicator is only slightly less than that with phenolphthalein and Cresol Red; with the new mixed indicator, however, the color change is sharper. In comparison with Kolthoff's indicator the new indicator is better both from the point of view of sensitivity and sharpness of color change.

The indicator is prepared by mixing aqueous solutions of 0.25% Indigo Carmine, 0.1% Cresol Red, and 0.1% Methyl Orange in the proportions of 2:2:1.

During titration in dilute solutions, 2-3 drops of mixed indicator solution are added per 100-150 ml of solution to be titrated. For detection of ethylene oxide, 2 drops of the indicator solution are added to 2-3 ml of 35% thiosulfate solution (or urotropine) followed by 1 drop of 0.02% acetic acid solution.

SUMMARY

A mixed color indicator for ethylene oxide detection has been prepared by mixing aqueous solutions of 0.25% Indigo Carmine, 0.1% Cresol Red, and 0.1% Methyl Orange in the proportions of 2:2:1.

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Received December 22, 1954

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REDUCTION OF NITROCYCLOHEXANE BY HYDRIODIC ACID AS A METHOD FOR QUANTITATIVE DETERMINATION OF THE FORMER

B. L. Moldavsky and I. I. Ivanova

We have found that nitrocyclohexane in its acid form (in alkaline solution) reacts with hydriodic acid and is reduced to cyclohexaneoxime: $C_6H_{10}NOOH + 2HI \rightarrow C_6H_{10}NOH + I_2 + H_2O$. This reaction can be used for the quantitative determination of nitrocyclohexane An aliquot (1-2 g) of nitrocyclohexane was dissolved in 70-80 ml of ethanol or methanol and to the solution obtained was added 10 ml of aqueous KOH (1:5) and the volume made up to 100 ml either with water or alcohol. 5 g of KI was introduced into the titration flask followed by 40 ml of water and 20 ml HCl (1: 2); 10 ml of the alkali-alcoholic solution of the nitrocompound was then added from a pipet dropwise, the titration flask being agitated continuously. After standing for a minute the contents of the flask were titrated with 0.1 N sodium thiosulfate. Results of such determinations are given in Table 1.

TABLE 1

Grams of nitrocyclohexane in 100 ml of solution	Solvent	Nitrocyclohexane found, in %
1.2316	C_2H_5OH	99.5
1.3281	C_2H_5OH	98.5
1.1828	C_2H_5OH	99.7
1.1762	CH_3OH	99.2
1.5236	CH_3OH	99.6

The course taken by the reduction of nitrocyclohexane to cyclohexaneoxime has been shown by isolation of cyclohexanone from the acidified reaction product after steam distillation. For this purpose about 5 g of nitrocyclohexane was dissolved in 20 ml aqueous KOH (1: 5). The solution obtained was added with stirring to an aqueous solution of KI (20 g in 50 ml water) and 60 ml HCl (1: 2). The iodine which was thereupon liberated was complexed by addition of sodium thiosulfate. After filtration the solution obtained was diluted with water and acidified with hydrochloric acid, and finally distilled. Cyclohexanone, the decomposition product of cyclohexaneoxime, was distilled over and removed by extraction with ether; it boiled at 153-154°. A mixed melting point of the paranitrophenylhydrazone prepared had a m.p. of 146°. A mixed melting point of the paranitrophenylhydrazone obtained in this way with the paranitrophenylhydrazone of cyclohexanone was also 146°.

This reaction is similar to Konovalov's reaction [1], which consists of the reduction of isonitrocyclohexane by means of $SnCl_2$ in hydrochloric acid:

$$C_6H_{10}NOOH + SnCl_2 + 2HCl \rightarrow C_6H_{10}NOH + SnCl_4 + H_2O$$

SUMMARY

Nitrocyclohexane in its acid form (in alkaline solution) reacts readily with hydriodic acid to give cyclohexaneoxime:

$$C_6H_{10}NOOH + 2HI \rightarrow C_6H_{10}NOH + I_2 + H_2O$$

This reaction can be used for quantitative determination of nitrocyclohexane.

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[1] M. I. Konovalov, J. Russ. Phys. Chem. Soc. 30, 960 (1898).

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BOOK REVIEWS

A. I. Busev, "Analytical Chemistry." Index to Literature Published in Russian during the period 1941-1952. Acad. Sci. USSR Press Moscow, 1956, 404 pp. Printing 2500. Price 24 roubles 40 kopecks. Bound.

The literature dealing with analytical chemistry is distributed among numerous chemical, physical, biological, agricultural, medical, geological, metallurgical, and other journals as well as in symposia, proceedings, transactions, bulletins, and reports. Such specialized journals as "J. Anal. Chem." and "Factory Labs." cover only a small amount of the relevant work (on account of the small size of such journals). This scattering of analytical work over such a large number of journals means that it is very difficult to use the results obtained and difficult to plan work along new lines. We are therefore glad to see the timely issue of this book of Busev's which was undertaken under the auspices of the Commission on Analytical Chemistry and the Institute of Scientific Information of the Acad. Sci. USSR. This book fills a gap in Russian reference literature on analytical chemistry.

The author has carried out a large amount of work in compiling and systematizing the literature on all questions dealing with the theory and practice of analytical chemistry including inorganic and organic analysis. The book includes books and journals published in Russian during the period January 1, 1941 to December 31, 1952, i.e., up to the appearance of the reference journal "Chemistry" of the Acad. Sci. USSR. The book refers to 8495 individual items. A scrutiny of the index did not lead to the detection of one omission, indicating the great care and high level of the book under review. About 10,000 surnames are included. The carefully compiled index allows one to find data on any particular subject rapidly. The book gives an exhaustive idea of the state of analytical chemistry in the Soviet Union during the period 1941-1955, both as a whole and with respect to individual directions along which this subject has developed.

From a polygraphic point of view the book is well done. Nevertheless some errors can be detected which should not be permitted in books of this type. E.g., 1051 is printed instead of 1951 in the bibliographical reference No. 1100, while in No. 8220 Tiscliuis is given instead of Tiselius; on p. 336, column 1, line 1 from the top, instead of Ryazanov, Rvanov is given; on p. 336, column 1, line 31 from the top, N. V. Molividova is given instead of N. V. Milovidova; on p. 357, column 3, line 9 from the top, So instead of Co. The number of such errors is small.

On closer scrutiny some omissions can be found; the following have been left out, for example: 1) T. F. Ivanova—Spectrographic Methods of Analyzing Ferrous Metals, Compiled by T. F. Ivanova (book) 1947, 40 pp with illustrations (Sci. Inst. No. 13); 2) V. K. Prokofiev—Spectrographic Analysis (of Metals) in the Practice of Factory Laboratories, Armaments 1941, No. 9 pp. 12-15; 3) G. Zavadsky, An Advanced Laboratory for Controlling the Quality of Oil and Fuel, Supplies for the Soviet Army 1951, No. 11 pp. 71-72; 4) P. F. Fedorov and V. V. Eremichev—Express Methods for the Complete Chemical Analysis of Martensite Slags— compiled by Fedorov and Eremichev, Moscow, 28 pages with illustration (Institute No. 13); 5) M. A. Mardanov—A Rapid Method for Quantitative Determination of Water in Spent Sulfuric Acid—Azerbaidzhan Pet. Econ. 1952, No. 9 (15) pp. 17-18; 6) Z. S. Mukhina and T. I. Sudarchikova—Polarographic Determination of Chromium as the Major Component of Chrome Baths, as well as Determination of Copper, Iron, and Lead as Impurities, Project No. 117 (Aviation Ministry of the USSR) Moscow, 1949 pp. 1-3.

Busev's book will no doubt become a standard reference book for a large number of analytical chemists in research and factory laboratories. Consequently it is to be hoped that there will soon be similar books covering the periods 1930-1940, and 1953-1956 since the reference journal "Chemistry" does not give a complete coverage of Russian literature.

N. A. Rudnev

I. M. Korenman, "Microcrystalloscopy." Moscow, State Chem. Press 1955, 431 pp. Printing 6,000. Price 15 roubles 50 kopecks.

Microchemical analysis is being more widely used from year to year. I. M. Korenman's valuable book is therefore very welcome.

The first part is devoted to general questions of microcrystalloscopic analysis, apparatus and technique being described in detail. The second part includes descriptions of a large number of reactions for cations and anions, and also for many organic compounds.

Methods for the analysis of metals, alloys, water and certain technically important materials are considered in the third part of the book. The comprehensive bibliography appended to each part is of considerable interest.

Despite the undoubted positive attributes of this good and interesting book of Korenman's, it is necessary to make some observations – for the most part on special questions.

In our opinion the chapter entitled "The technique of microcrytalloscopic analysis (pp. 11-24) is not so well written as the others. Here the author discusses the effect of various factors on the form, size, and composition of crystals. Nevertheless, after reading this material one must unwillingly conclude that in most cases no definite rules exist. Thus, crystals of $CaC_2O_4 \cdot 3H_2O$ precipitated by oxalic acid and ammonium oxalate (Figs. 25, 26, p. 20) have different forms. What does this depend on?, why should the composition of the precipitates be the same? Neither here nor in many other cases does Korenman give any explanation. Several such instances can be quoted.

We think that in general this chapter on "The technique of microcrystalloscopic analysis" is incorrect. Perhaps one should refer e.g., the cases cited (p. 22) of the appearance of a rose or reddish color of crystals of $BaSO_4$ and $PbSO_4$ precipitated in the presence of $KMnO_4$ to questions of method? Presumably, the adsorption, and of course coloration as a result of adsorption of MnO_4, is characteristic not only for the sulfates indicated, but also for a number of other precipitates. The author keeps quiet about this.

The list given on p. 18 of materials which slow down precipitation evokes an immediate protest. Naturally, changes in pH can affect not only the crystal size but also their shape – sometimes to a considerable extent. The author, however, gives no explanation why concentrated H_2SO_4 and concentrated HCl slow down precipitation of strontium and calcium sulfates, while HCl does not affect precipitation of barium and lead sulfates. The effect of materials which slow down precipitation has not been given any theoretical foundation.

One cannot possibly agree with the statement that "one can increase the *sensitivity* (the emphasis is mine O. D.) of a reaction by 20-50%" if one only makes a comparison with control tests (p. 104). In the 1947 edition, a similar statement was backed up by a suitable table. It is not a question of increasing the sensitivity of a reaction, but of the low concentrations at which it is more convenient to carry out tests in parallel with a control. The principles underlying classification of cations should have been dealt with in more detail. Why has Mg^{2+} been ommitted in this classification (p. 117)?

The chapter on anions does not contain information on new sensitive microcrystalloscopic reactions for: CN^- with alloxane, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ with hexaminocobaltinitrate, etc.

The material included in the very valuable chapter devoted to the microcrystalloscopic reactions of organic compounds (pp. 258-314), is, unfortunately, not systematized at all. The chapter starts, for some reason, with a discussion of aromatic hydrocarbons and immediately the author starts dealing with halowax (?). After carbohydrates, to which the author only allocates one page – p. 269 – the acids are dealt with. The number of literature references is not enough in this section. The classification of alkaloids (incomplete) given on p. 296 is not used subsequently.

The book would be considerably improved if the most important reactions for organic compounds were tabulated as in the case of anions and cations. Analysis of minerals (315-316) is dealt with completely inadequately. For some metals, the author on p. 316 has confined himself only to separate reactions; this is clearly not enough.

Certain inaccuracies have crept into the book. This is true of the separation of the hydrated oxides of aluminum, chromium, and iron from Mn^{2+}, and Zn^{2+} by means of ammonia (p. 153). The principles underlying the construction and operation of the microcentrifuge (p. 54, Fig. 78) are not made clear. There is no explanation why a mixture of $Ca(CH_3COO)_2$ and NH_4OH is used for detecting CO_2 instead of $Ca(OH)_2$. Presumably, by using KI + starch one should be able to detect not only the gaseous materials given in Table 7, but all other oxidizing agents. Detection of iodine by starch and KI (?) would then appear to be strange.

The subdivision of reactions for NH_4^+ and NH_3 seems somewhat artificial (pp. 358-359). It is doubtful whether it is possible to effect complete separation of all the alkaline-earths from magnesium by means of H_2SO_4. Detection of chlorides, bromides, and iodides when they are simultaneously present is possible without using Pt^{4+} (p. 236).

It would have been much better if the author had consistently used the same word throughout for the same compound. Thus "sulfuric acid" is used sometimes and the formula H_2SO_4 used at other times. The cation in the acetates is sometimes written before and other times written after the acid radical e.g., CH_3COONH_4 and $Ba(CH_3COO)_2$ (see note 1, p. 338) etc.

The number of molecules of water of crystallization is sometimes but not always indicated; e.g., for $K_2C_2O_4$ (p. 342). Incorrect names are given for $K_3[Co(CN)_6]$ (pp. 164 and 343) and for $Na_2HPO_4 \cdot 12H_2O$ (p. 347).

Descriptions of the loretine reaction for Ca^{2+}, the acridine hydrochloride reaction for rhenium and of several other important reactions are absent. Taking into account the small number of reactions for Cr^{2+} (p. 150), a more detailed description should have been given of the formation of the characteristic crystals of alum (p. 154), where the inclusion of a photograph or diagram of the respective crystals would have been very useful, although it should also be added that these crystals do not invariably have the form of hexagons or rhombs.

We feel that it should be possible to simplify the analysis of mixtures of Ag^+, Pb^{2+}, and Hg_2^{2+}, (p. 109), by separating Pb^{2+} as $PbSO_4$ or by dissolving $PbCl_2$ in hot water. AgCl could be separated from Hg_2Cl_2 by means of NH_3.

Should one recommend that in all cases liquids should be blown out of capillaries (p. 39)? Is it necessary to state that determination of the reaction of a medium (p. 63) can be carried out by means of other things and not only by litmus?

In the scheme for identification of some mineral dyes (the Augusta scheme) the chemical composition of the dyes should have been given throughout. As it is, this has only been done for some of them, mainly white and yellow dyes.

The magnification employed should have been stated on each diagram in every case, and not just now and again.

There are some misprints. After section 4 on the reactions for Ca^{2+} we have section 6 (p. 143). The reference (p. 146) to the microreaction for Ba^{2+} on p. 173 is incorrect, as well as that to the reaction for oxalates on p. 250 (see p. 427). The sulfates relate to the III and VI groups of anions (p. 230) and not to the sulfites mentioned.

These mistakes in no way diminish the value of the book. This very important and well written book of Korenman's is a valuable contribution to chemical science and will find plenty of readers.

O. K. Dobrolyubsky

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CHRONICLE

THE INTERNATIONAL CONGRESS OF ANALYTICAL CHEMISTRY

THE XVth CONGRESS OF THE INTERNATIONAL UNION OF THEORETICAL AND APPLIED CHEMISTRY (ANALYTICAL CHEMISTRY DIVISION)

The second congress on Analytical Chemistry organized by the International Union on Pure and Applied Chemistry was held on 8-16th September 1956 in Lisbon. About 700 representatives from 65 countries were present at the congress.

A large number of reports dealing with current problems of modern analytical chemistry were read at the plenary and section sessions.

The chairman of the analytical chemistry division, Prof. I. M. Kolthoff (University of Minnesota–Minneapolis), read a very interesting lecture on the subject of "The Interpretation of Alkalimetric and Acidimetric Titrations in Glacial Acetic Acid."

The lecturer set forth the theory of the problem with great thoroughness.

Prof. A. Tiselius (Biokemiska Institution - Uppsala), one of the foremost specialists on methods for studying high-molecular compounds, delivered a lecture on "Analysis of High Molecular Weight and Colloidal Systems by Means of Some Physicochemical Methods."

A. I. P. Martin (National Institute for Medical Research – London), the founder of the chromatographic method of analyzing gases, reported on "Gas Liquid Chromatography – Recent Developments." Finally, Prof. Burnel Marti (Madrid University) read a paper on "Current Problems in the Analytical Chemistry of Traces of Certain Elements," and Prof. G. Charlot (Ecole Sup. de Physique et de Chimie Industrielles– Paris) on Analyticochemical and Electrochemical Reactions."

The paper read by Prof. Feigl (Lab. Prod. Mineral–Rio de Janeiro) entitled "Qualitative Organic Analysis with Special Reference to Trace Analysis" evoked considerable interest. Prof. Feigl reported on a number of qualitative reactions for secondary alcohols, sulfur, carboxyl compounds, phenols, secondary amines, and other materials. The lecture was accompanied by demonstrations of these reactions.

Of a large number of lectures delivered at sessions of particular were the following: Prof. K. Kruze "Oscillometric Titration in Analytical Chemistry;" Prof. G. Dankerts –"Progress in the Field of Quantitative Molecular Analysis;" Prof. G. Schwarzenbach – "Organic Reagents in Analysis;" G. Vernimont "Bases of Interpreting Analytical Results;" Prof. M. K. Tsakherli "Methods of Separation by Adsorption;" Prof. Herculiano da Karvalio "Evolution of Analytical Chemistry;" Prof. I. R. I. Forbes, "Standardization of Analytical Methods and its Problems;" Prof. I. Debied, "Realizing the Research Program of Studies in the French Commissariat of Atomic Energy."

All reports read at the congress will be printed in the immediate future in the publication "Experimentation" (Birkhauser – Basel).

It was made quite manifest at this conference again that the main directions taken by analytical chemistry – in referring to objects of investigation – are determination of traces by all methods possible; while as for methods, then complexometry, optical methods and reactions in nonaqueous media seem to be the main directions taken. The rapid development of radiochemical methods of analysis should also be emphasized.

The Congress noted with regret the absence of representatives from the Soviet Union.

An exhibition was staged at the Lisbon Polytechnical Institute for participants in the congress, at which was shown modern analytical apparatus made by American, English, French, and West German firms. Of special interest were new Sartorius balances and completely automatic apparatus for analyzing gases chromatographically.

Numerous excursions, meetings, and receptions were organized; participants at the congress were also given the opportunity to visit an ultra-modern automatized petroleum refinery with a catalytical cracker at Lisbon.

The congress expressed the wish that there should be closer contact between analytical chemists and freer exchange of opinions and ideas.

E. Minchevsky (Institute of Nuclear Studies,
Polish Academy of Sciences, Warsaw).

THE FIRST CONFERENCE ON THE APPLICATION OF ORGANIC REAGENTS IN ANALYTICAL CHEMISTRY

From November 27-30, 1956 a conference was held at Moscow on the application of organic reagents in analytical chemistry; it was organized by the Commission on Analytical Chemistry of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR.

About 750 representatives from 250 research institutes, universities, and factory laboratories were present. 240 delegates came from Leningrad, Kazan, Novosibirsk, Kiev, Dnepropetrovsk, Kharkov, Tashkent, Alma-Ata, Norilsk, Ust-Kamenogorsk and other cities. Some foreign scientists were also present: Doctor A. Okach and Doctor Prshibl from Czechoslovakia, Doctor Dragulescu from Rumania, Doctor E. Minchevsky from Poland and Doctor Lyan Shu Chuan from China.

At the conference reports were heard which dealt with the theory of the action and development of organic reagents, and also with studies on the practical application of organic reagents for solving special problems in analytical chemistry. Some of the reports dealt with the state of production of organic reagents.

In a review, V. I. Kuznetsov dealt with the development of the theory of organic reagents, successes achieved by means of such reagents and the prospects for their use in future; V. M. Peshkova reported on the use of organic reagents in spectrophotometry, while S. I. Sinyakova read a paper on the use of organic reagents in polarography. In F. M. Shemyakin's report the classification of organic reagents used in chromatography was discussed, and certain lines for future development in chromatography were proposed.

Questions relating to the theory of the action of organic reagents were dealt with in the following reports: The mechanism of the acid decomposition of inner complex salt – V. I. Kuznetsov; Chromophores and chromophoric groups – V. A. Izmailsky. The displacement of the maximum on the absorption spectra of interaction products of organic reagents with metals – A. I. Cherkesov. V. M. Peshkova, V. M. Bochkova, and A. P. Zozylya communicated their results of studies on the stability of metal dioximates in relation to the structure of the dioxime molecule.

Some reports were devoted to photometric methods of determining individual elements by means of organic reagents. Considerable interest was evoked by the report of S. I. Burmistrov on a new color reaction for pyrosulfates carried out by means of nitrosophenol, by means of which it is possible to detect pyrosulfates in the presence of sulfates and bisulfates. The practical value of colored solid phase reactions for volumetric analysis was demonstrated by V. P. Zhivopistsev, who took as an example the quantitative determination of small amounts of zinc by titration with an organic dye; the latter forms with zinc, in the presence of cyanogen, a sparingly soluble salt whose color differs considerably from the color of the original dye. A. I. Busev read a report on a selective complexonometric method of determining bismuth, using 1-(s-pyridyl azo)-2-naphthol as indicator. A number of reports were devoted to the photometric determination of palladium, tungsten, aluminum, and sulfate ions by means of organic reagents (A. K. Babko and L. V. Markova, K. E. Kleiner and A. Kh. Klibus, V. M. Peshkova and V. I. Shlenskaya, L. A. Molot, I. S. Mustafin, and N. S. Frumina).

Of considerable interest also were reports dealing with new organic reagents: organic substituted sulfuric, selenious, and tellurious acids (A. I. Alimarin, V. S. Sotnikov, and S. S. Alikberov); dialkyl and diaryldithiophosphoric acids (A. I. Busev and M. I. Ivanyutin); selenourea (A. T. Pilipenko and I. P. Sereda); 8-mercaptoquinoline (V. I. Kuznetsov, Yu. A. Bankovsky, and A. F. Ievinsh); dithizone analogs (I. B. Suprunovich).

Several reports were devoted to the determination of toxic materials in air; these were of importance to workers working in factories where such compounds are produced.

The Czech representatives had some interesting reports to deliver. R. Pribil reported on the possibility of using new and hitherto not reported metal indicators which he had discovered for complexonometric determination of elements. The report was accompanied by experiments demonstrating the special features of the new indicators. A. Okach's report dealt with determination of titanium in steels.

Reports by R. L. Globus, A. T. Pilipenko and S. I. Burmistrov were concerned with the question of producing and standardizing organic reagents. At the conference an exhibition was staged of organic reagents produced by Russian industry.

Lively discussions ensued at the conference. A number of resolutions were adopted which dealt with the development of the theory of organic reagents and their practical application in analytical chemistry. The need for extending the variety of organic reagents produced was emphasized, particularly special reagents for determining rare and scattered elements; the need for producing more special apparatus and materials was also stressed. The conference recommended publication of a series of monographs dealing with the theory and application of organic reagents.

Z. I. Podgaiskaya and L. V. Seryakova

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EXTRACTION AS A METHOD OF PHYSICOCHEMICAL ANALYSIS

I.M. Korenman and F.R. Sheyanova

The N.I. Lobachevsky, Gorky State University.

In recent years extraction has been used in conjunction with determination of optical density as a physicochemical method of analysis, for establishing the composition of certain dithizonates [1-3]. The method in outline is as follows: various volumes of an aqueous solution of the appropriate salt and of a dithizone solution of equal molar concentration are shaken with an organic solvent which is immiscible with water. The optical density of the extract is then determined after it has been diluted to a constant volume with pure solvent. Judging by experimental data this method gives good results, though there are certain peculiarities. Determination of composition on the basis of the intensity of the color of a mixture of different volumes of aqueous solutions of two components of equal molar concentration does not require additional hypotheses since, on mixing, a homogenous solution is obtained. This method has been considered in detail in the work of Babko [4-6], Pilipenko [7], and Komar [8]. In the case of immiscible solutions of both components, although the sum of the volumes of both phases is the same in all tests, nevertheless the ratio of the volumes alters, which cannot fail to be reflected in the amount of reaction product extracted. The technique adopted above, of diluting different amounts of the organic solvent to constant volume, leads to differing degrees of dilution and to certain changes in the absolute value of the optical density. In general, it is difficult to affirm how far these changes may affect the general character of the results obtained. Accordingly, we thought it necessary to carry out a number of calculations together with appropriate experimental work, in order to establish the relation between the amounts of cation and reagent taken and the amount of extracted reaction product.

First of all, let us consider the simplest case where the extracted compound of type MeR is formed between cation Me^+ and reagent HR, the latter being a monobasic acid:

$$HR \rightleftarrows H^+ + R^-, \tag{1}$$

whose dissociation constant is given by:

$$\frac{[H^+][R^-]_W}{[HR]_W} = K_{HR} \tag{2}$$

The inner complex compound MeR which is formed dissociates to a certain extent in aqueous solution:

$$MeR \rightleftarrows Me^+ + R^- \tag{3}$$

$$\frac{[Me^+]_W[R^-]_W}{[MeR]_W} = K_{MeR}. \tag{4}$$

The distribution coefficient of compound MeR between water and organic solvent is equal to:

$$\frac{[MeR]_0}{[MeR]_W} = K_1, \tag{5}$$

where $[MeR]_W$ is the equilibrium concentration of the extracted compound in the aqueous phase: $[MeR]_0$ is the equilibrium concentration of the extracted compound in the organic solvent.

The distribution coefficient of the reagent is equal to:

$$\frac{[HR]_0}{[HR]_W} = K_2. \qquad (6)$$

On dividing Equation (2) by Equations (4) and (6) multiplying by Equation (5) we get:

$$\frac{[MeR]_0 [H^+]_W}{[Me^+]_W [HR]_0} = \frac{K_{HR} \cdot K_1}{K_{MeR} \cdot K_2} = K. \qquad (7)$$

Equation (7) expresses the equilibrium constant of the process

$$\underset{W}{Me^+} + \underset{0}{HR} \rightleftarrows \underset{0}{MeR} + \underset{W}{H^+}.$$

It is the equilibrium and not the initial concentrations Me^+ and HR which enter into Equation (7). Expressing the latter by c_{Me^+} and c_{HR} we find that:

$$[Me^+] \approx c_{Me^+} - [MeR]_0$$
$$[HR] \approx c_{RH} - [MeR]_0.$$

Accordingly, Equation (7) may be rewritten in the form:

$$\frac{[MeR]_0 [H]^+}{(c_{Me^+} - [MeR]_0)(c_{HR} - [MeR]_0)} = K. \qquad (8)$$

Let us study Equation (8) under conditions where extraction is carried out from a buffered solution, i.e., for constant hydrogen ion concentration.

In this case:

$$\frac{[MeR]_0}{(c_{Me^+} - [MeR]_0)(c_{HR} - [MeR]_0)} = \frac{K}{[H^+]} = \frac{1}{N}, \qquad (9)$$

where

$$N = \frac{[H^+]}{K}$$

Solving this equation with respect to $[MeR]_0$, we get:

$$[MeR]_0 = \frac{N + c_{HR} + c_{Me^+} \pm \sqrt{(N + c_{HR} + c_{Me^+})^2 - 4c_{HR} \cdot c_{Me^+}}}{2}. \qquad (10)$$

This equation takes on a simpler form for cases where $N = c_{HR} + c_{Me^+}$, or when N is considerably greater or smaller than $c_{HR} + c_{Me^+}$ (smaller values can be neglected).

a) $N = c_{HR} + c_{Me^+}$

$$[MeR]_0 = \frac{2(c_{HR} + c_{Me^+}) \pm \sqrt{4(c_{HR} + c_{Me^+})^2 - 4c_{HR}\, c_{Me}}}{2} = \qquad (11)$$
$$= (c_{HR} + c_{Me^+}) \pm \sqrt{c^2_{HR} + c^2_{Me^+} + c_{HR} \cdot c_{Me^+}}.$$

A real value is only obtained when there is a minus sign in front of the square root; otherwise $[MeR]_0$ is greater than c_{Me^+} or c_{HR}, which, of course, is impossible.

b) $N << c_{HR} + c_{Me^+}$

$$[MeR]_0 = \frac{(c_{HR} + c_{Me^+}) \pm \sqrt{(c_{HR} + c_{Me})^2 - 4c_{HR} \cdot c_{Me}}}{2} =$$

$$= \frac{(c_{HR} + c_{Me^+}) \pm (c_{Me^+})}{2}. \qquad (12)$$

Only the smaller of two possible values can have a real value. For $c_{HR} < c_{Me^+}$ there should be a plus sign in front of the square root, while for $c_{HR} > c_{Me^+}$ the sign in front of the square root should be minus. Otherwise, $[MeR]_0$ will be greater than either c_{Me^+} or c_{HR}.

c) $N >> (c_{HR} + c_{Me^+})$

$$[MeR]_0 = \frac{N \pm \sqrt{N^2}}{2} = 0 \text{ or } N. \qquad (13)$$

It is not difficult to see that only a value practically equal to zero will be real. The concentration of extracted material cannot be equal to N. If one assumes that $[MeR]_0 = N$, then according to the condition $[MeR]_0 >> c_{HR} + c_{Me^+}$, which is completely impossible. Accordingly, under such conditions there will be practically no extraction.

Equations (11) and (12) enable one to calculate the concentration of extracted MeR in relation to the ratios of the original concentrations Me^+ and HR, and under conditions such that the sum of their concentrations is constant.

Table 1 contain values for the calculated concentration $[MeR]_0$

TABLE 1
Values of $[MeR]_0$ for Various N (it is assumed that $N = \frac{[H^+]}{K} = 10^{-(n-1)}$)

c_{HR}	c_{Me^+}	$c_{HR} : c_{Me^+}$	$N<(c_{HR}+c_{Me^+})$	$N-(c_{HR}+c_{Me^+})$	$N>(c_{HR}+c_{Me^+})$
			Value of $[MeR]_0$		
$1 \cdot 10^{-n}$	$9 \cdot 10^{-n}$	1 : 9	$1 \cdot 10^{-n}$	$0.5 \cdot 10^{-n}$	zero
$2 \cdot 10^{-n}$	$8 \cdot 10^{-n}$	1 : 4	$2 \cdot 10^{-n}$	$0.85 \cdot 10^{-n}$	»
$3 \cdot 10^{-n}$	$7 \cdot 10^{-n}$	1 : 2.3	$3 \cdot 10^{-n}$	$1.1 \cdot 10^{-n}$	»
$4 \cdot 10^{-n}$	$6 \cdot 10^{-n}$	1 : 1.5	$4 \cdot 10^{-n}$	$1,3 \cdot 10^{-n}$	»
$5 \cdot 10^{-n}$	$5 \cdot 10^{-n}$	1 : 1	$5 \cdot 10^{-n}$	$1.35 \cdot 10^{-n}$	»
$6 \cdot 10^{-n}$	$4 \cdot 10^{-n}$	1 : 0.66	$4 \cdot 10^{-n}$	$1.3 \cdot 10^{-n}$	»
$7 \cdot 10^{-n}$	$3 \cdot 10^{-n}$	1 : 0.46	$3 \cdot 10^{-n}$	$1.1 \cdot 10^{-n}$	»
$8 \cdot 10^{-n}$	$2 \cdot 10^{-n}$	1 : 0.25	$2 \cdot 10^{-n}$	$0.85 \cdot 10^{-n}$	»
$9 \cdot 10^{-n}$	$1 \cdot 10^{-n}$	1 : 0.11	$1 \cdot 10^{-n}$	$0.5 \cdot 10^{-n}$	»

These results are shown graphically in Fig. 1.

Table 1 and Fig. 1 enable us to draw a number of conclusions. Extraction is more complete the smaller the value of N. At low values of N it is possible to achieve practically complete extraction of MeR by the organic solvent, under conditions such that the initial concentration of reagent HR is equivalent to or greater than the initial concentration of cation Me^+ in solution.

On the other hand, at very high values of N, extraction is hardly observed at all.

Since $N = \frac{[H^+]}{K}$, then, with decreasing hydrogen ion concentration (increasing pH) the value of N decreases, leading to a more complete extraction. This means that increasing the pH should lead to an improvement in extraction conditions and to fuller extraction (Fig. 2, line 1). Nevertheless, the extent of extraction increases only to a certain limit; subsequently, further increase in the pH leads to a lower percentage extraction (Fig. 2, line 2). This latter is explained by the fact that at high pH the reaction product MeR starts to break down:

$$MeR + OH^- \rightarrow MeOH + R^-.$$

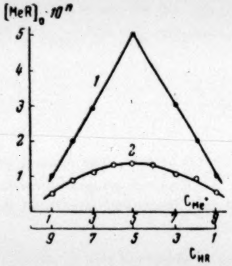

Fig. 1. Relation between amount of MeR extracted, the ratio of the concentrations of HR and Me^+, and the value of N:
1) $N \ll (c_{HR} + c_{Me^+})$; 2) $N = (c_{HR} + c_{Me^+})$

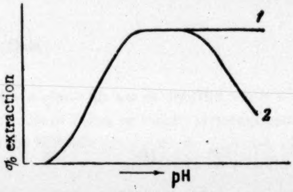

Fig. 2. Relation between percentage extraction and pH.

The hydroxide (or basic salt) is not extracted, the amount of MeR decreases, and consequently the amount of material which goes into the layer of organic solvent also decreases. For a constant value for the sum of the initial concentrations Me^+ and HR, maximum extraction is observed in this case when the ratio of these concentrations is equal to the ratio of the amounts of Me^+ and R^- in the compound obtained (in the given case 1:1). The latter is confirmed by the fact that it is possible to use extraction for determining the composition of the compounds formed.

Determination of the composition of certain compounds extracted by organic solvents can be carried out by the following methods.

First Method. Different volumes of an aqueous solution of test cation, and a non-aqueous solution of the reagent, at equal molar concentrations of cation and reagent are shaken up together. The total volume is a constant for the whole series. This method has been successfully used by Babko and his co-workers for determining the composition of dithizonates [1 - 3].

Second Method. Equal volumes of the solution indicated in the first method are shaken up. The concentration of both solutions is different, but the total number of moles of reactants is kept constant throughout the series.

In order to find out which of these two methods is the more correct, it is necessary to transform Equation (9) somewhat.

The concentrations of the components, which can otherwise be represented as ratios of the absolute amounts to the appropriate volumes, enter into Equation (9).

In this case, Equation (9) assumes the following form:

$$\frac{MeR_0\, V_0 \cdot V_n}{(Me^+ - MeR_0)(HR - MeR_0) \cdot V_0} = \frac{1}{N}, \tag{14}$$

where MeR_0 is the extracted amount of reaction product in millimols; Me^+ – the initial amount of cation in millimols; HR – the initial amount of reagent in millimols; V_0 – the volume of the non-aqueous solvent in ml; and V_W the volume of the aqueous phase in ml.

Denoting V_W/V_0 by r, and solving Equation (14) with respect to MeR_0, we get:

$$MeR_0 = \frac{Me^+ + HR + NV_0r - \sqrt{(Me^+ + HR + NV_0r)^2 - 4Me^+HR}}{2}. \tag{15}$$

In this way we get an equation similar to equation (10), in which concentrations are replaced by the absolute amounts of components. This equation is convenient in that the volumes of the aquous and non-aqueou phases come into it. By analogy with Equation (11-13) we see that if $NV_0 r >> (Me^+ + HR)$, then there is practically no extraction. When $NV_0 r << (Me^+ + HR)$, the first member can be neglected; in this case variations in the volumes of both layers has hardly any effect on the absolute amount of extracted reaction product. Finally, for $NV_0r \approx (Me^+ + HR)$ there may occur a change in the absolute amount of extracted reaction product on changing the volumes of the phases.

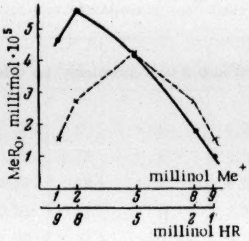

Fig. 3. Amount of extracted reaction product in relation to the volumes of the aqueous and nonaqueous phases :

——— ——— different volumes of both phases
- - - - - - - - - equal volumes of both phases.

By making use of equation (15), we can calculate the amount of extracted reaction product on changing the volumes of both phases, and for constant volumes. In both cases the initial amounts of the components change equally. Let us assume that in both layers there is always 10^{-3} mol of Me^+ and HR, and that $N = 10^{-3}$ (Tables 2 and 3). We see that for different volumes of the phases there can be observed an essential change in the character of the curve, on the basis of which it is possible to make incorrect conclusions. Consequently the first method should not be used except when the sum of the amounts of cation and reagent is equal to $NV_0 r$.

The second method, even in this case, gives completely correct results. Since the value of N is not always known, it is obvious that the second method should be given preference as applicable for any values of N. All the same the first method is considerably simpler to carry out in practice. This method can be used if the tests are carried out for two or three different values of $(c_{Me^+} + c_{HR})$. If, when this is done, similar results are obtained, this means that $N < (c_{Me^+} + c_{HR})$; that is, conditions for which the first method is applicable are observed. In practice, reactions with divalent cations leading to the formation of inner complex compounds of the composition MeR_2 are of great importance.

$$\frac{[Me^{2+}][R^-]^2}{[MeR_2]_W} = K_{MeR_2}, \tag{16}$$

for which the distribution constant between two solvents is equal to

$$\frac{[MeR_2]_0}{[MeR_2]_W} = K_1. \tag{17}$$

TABLE 2

Amount of Extracted Reaction Product in Relation to the Volume of the Aqueous and Nonaqueous Phases.

Me^{+} in millimols	HR in millimols	V_W in ml	V_O in ml	r	$V_* r$	MeR_O in millimols
$1\cdot10^{-4}$	$9\cdot10^{-4}$	1	9	0,11	0.99	$4.6\cdot10^{-6}$
$2\cdot10^{-4}$	$8\cdot10^{-4}$	2	8	0,25	2	$5.5\cdot10^{-6}$
$5\cdot10^{-4}$	$5\cdot10^{-4}$	5	5	1	5	$4.2\cdot10^{-5}$
$8\cdot10^{-4}$	$2\cdot10^{-4}$	8	2	4	8	$1.8\cdot10^{-5}$
$9\cdot10^{-4}$	$1\cdot10^{-4}$	9	1	9	9	$9\cdot10^{-6}$
$1\cdot10^{-4}$	$9\cdot10^{-4}$	5	5	1	5	$1.5\cdot10^{-5}$
$2\cdot10^{-4}$	$8\cdot10^{-4}$	5	5	1	5	$2.75\cdot10^{-5}$
$5\cdot10^{-4}$	$5\cdot10^{-4}$	5	5	1	5	$4.2\cdot10^{-5}$
$8\cdot10^{-4}$	$2\cdot10^{-4}$	5	5	1	5	$2.75\cdot10^{-6}$
$9\cdot10^{-4}$	$1\cdot10^{-4}$	5	5	1	5	$1.5\cdot10^{-6}$

By dividing the square of Equation (2) by Equation (16) and multiplying by Equation (17), we get:

$$\frac{[MeR_2]_0\,[H^+]^2}{[Me^{2+}]\,[HR]_0^2} = \frac{K_1}{K_2} = \frac{K^2_{HR}}{K_{MeR_2}} = K'. \tag{18}$$

We then replace equilibrium concentrations of Me^{2+} and HR by their initial concentrations; for this we take into account that

$$[Me^{2+}] \approx c_{Me^{2+}} - [MeR_2]_0$$
$$[HR]_0 \approx c_{HR} - 2\,[MeR_2]_0.$$

On doing this we get, instead of Equation (18)

$$\frac{[MeR_2]_0}{(c_{Me^{2+}} - [MeR_2]_0)(c_{HR} - 2\,[MeR_2]_0)^2} = \frac{K'}{[H]^2}\,\frac{1}{N'}. \tag{19}$$

After a number of transformations we get an equation of the third degree:

$$4\,[MeR_2]_0^3 - 4\,[MeR_2]_0^2\,(c_{Me^{2+}} + c_{HR}) + [MeR_2]_0\,(4c_{Me^{2+}}\cdot c_{HR} + \\ + c_{HR} + N') - c_{Me^{2+}}\cdot c^2_{HR} = 0. \tag{20}$$

From what has been said above we know that extraction is best carried out at low values of N'; consequently, in order to simplify calculations, this factor can be neglected. Further, the total concentration of Me^{2+} and HR should be constant; assuming it be unity we get

$$4\,[MeR_2]_0^3 - 4\,[MeR_2]_0^2 + [MeR_2]_0\cdot(4c_{Me^{2+}}\cdot c_{HR} + c^2_{HR}) - c_{Me^{2+}}\cdot c_{HR} = 0. \tag{21}$$

On solving this equation with respect to the concentration of MeR_2, we come to the conclusion that for a constant total of $c_{Me^{2+}}$ and c_{HR}, the maximum amount of extracted MeR_2 will be observed at $c_{Me^{2+}} = 0.33$ and $c_{HR} = 0.66$, i.e., for a ratio of 1:2 (Table 3, Fig. 4).

It is obvious that maximum extraction of the compound Me_nR_m for a constant total of the initial concentrations of Me^{m+} and H_nR, will be observed under conditions such that $c_{Me^{m+}} : c_{H_nR} = n:m$.

The results obtained by calculation permit one to conclude that for low values of N, the amount of extracted reaction product, when excess reagent is used, depends only on the initial concentration of cation in solution, i.e.,

$$[\mathrm{MeR}_n]_0 = c_{\mathrm{Me}^{n+}}. \tag{22}$$

On the other hand when there is a deficit of reagent (or when excess cation is present) the amount of extracted reaction product is limited by the amount of reagent, viz.

$$[\mathrm{MeR}_n]_0 = \frac{c_{\mathrm{HR}}}{n}. \tag{23}$$

As already pointed out, extraction can be used succesfully for determining the composition of certain dithizonates.

TABLE 3

Values of $[\mathrm{MeR}_2]_0$ for Various Ratios of Initial Concentrations of Me^{2+} and HR.

$c_{\mathrm{Me}^{2+}}$	c_{HR}	$c_{\mathrm{Me}^{2+}} : c_{\mathrm{HR}}$	$[\mathrm{MeR}_2]_0$
0.20	0.80	1 : 4	0.20
0.25	0.75	1 : 3	0.25
0.33	0.66	1 : 2	0.33
0.50	0.50	1 : 1	0.25
0.66	0.33	1 : 0.5	0.165

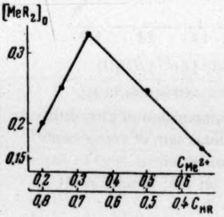

Fig.4. Values of $[\mathrm{MeR}_2]_0$ for Various Ratios of the Concentrations of Me^{2+} and HR.

The calculations which we have adduced show that, in principle, it is possible to determine other extractable compounds apart from dithizonates by the extraction technique. The authors quoted above [1-3] determined composition on the basis of the optical density of the extracted reaction product. It is understandable that such a method is only suitable for studying colored compounds. When we deal with solutions of low concentrations, and the color obtained has a low intensity or when the compounds are colorless, it is possible to use radioactive indicators and determine the amount of extracted compound radiometrically. As a result of the high sensitivity of such a technique one should get satisfactory results for determination of composition, even when working with solutions at low concentrations.

In order to confirm our ideas we carried out a series of radiometric determinations of the composition of certain compounds which are extractable by organic solvents. For comparison with published results, we, in the first series of tests, studied the composition of the dithizonates of zinc, cobalt, and mercury as well as that of zinc hydroxyquinolate. As pointed out already, composition can be determined by two methods. We decided that it would be more expedient to use the second method.

The technique and procedure used are self evident from the results which we have given for the determination of the composition of zinc dithizonate. A solution of zinc nitrate containing the radioactive isotope Zn^{65} and a solution of dithizone in chloroform were prepared. The concentrations of both components were varied within the limits 10^{-6} - 10^{-7} mol/liter. At such concentrations, and using such small volumes of the respective solutions, measurement of the optical density is hardly possible. Radiometric determination of the amount of extracted product does not present any particular difficulties.

To a known amount of zinc salt contained in a test tube with a ground glass stopper was added 1 ml of buffer solution* and enough water to make the total volume of the aqueous layer 3 ml. Aliquots of dithizone solution in chloroform were then added, together with some pure chloroform, so that the total final volume of the non-aqueous phase was also 3 ml. The contents of the test tubes were agitated by means of an electric stirrer until equilibrium had been attained (this point was ascertained in special tests) and then centrifuged.** 0.5 ml of the chloroform layer was taken and placed on a filter paper which was then dried and the activity determined. From the activity of the sample and that of a standard it was then easy to determine the content of zinc dithizonate in the organic layer. The composition of zinc dithizonate was studied in relation to the pH of the solution (Table 4, Fig. 5).

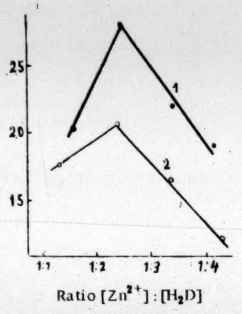

Fig. 5. Composition of zinc dithizonate; total sum of components 0.2 μ mol/6 ml: 1) tests at pH 5.8; 2) tests at pH 10

The results given in Table 4 and Fig. 5 enable one to conclude that, independently of the pH of the medium, the ratio Zn^{2+} : H_2D during formation of dithizonate is equal to 1:2; consequently, an acid salt of the composition $Zn(HD)_2$ is formed.

Similar results were obtained during a study of the composition of cobalt dithizonate. Experiments were carried out with a solution of cobalt nitrate containing the Co^{60} isotope (Table 5, Fig. 6).

Table 5 shows that in this case the acid salt $Co(HD)_2$ is formed.

Determination of the composition of mercury dithizonate was also of interest. According to published results [9], it might be postulated that the composition of mercury dithizonate depends on the pH of the medium. In acid solution one should get an acid salt of dithizone, while in an alkali medium the neutral salt should be formed. The composition of mercury dithizonate was determined at concentrations of the components equal to $10^{-6}-5\cdot10^{-7}$ mol/liter (Table 6, Fig. 7).

TABLE 4

Composition of Zinc Dithizonate

Content of components in μmol/3 ml		Ratio $Zn^{2+}:H_2D$	Specific activity in impulses/ /minute per γ Zn^{2+}	pH of the medium					
				4.2	5.8	7.6	10	11	12
Zn^{2+}	H_2D			Amount of zinc extracted in γ					
1	1	1:1	93	17.5	19	20.0	15.1	13.8	13.7
0.67	1.33	1:2		19.8	25.8	28.4	21.8	21.0	21.0
0.5	1.5	1:3		18.6	20.0	24.2	19.4	19.2	19.3
0.4	1.6	1:4		18	19.1	21.3	17.4	17.0	17.1
0.1	0.1	1:1	180	–	1.7	2.4	1.9	1.2	1.2
0.067	0.133	1:2		–	2.0	2.9	2.8	2.3	2.4
0.05	0.15	1:3		–	1.6	2.6	2.3	1.9	1.8
0.04	0.16	1:4		–	2.2	2.2	2.0	1.6	1.6

It is not difficult to notice that the composition of the mercury dithizonate depends on the pH of the medium and that in acid and neutral media $Hg(HD)_2$ is formed, while in alkali media (pH 9.8) the neutral salt is formed. It should be pointed out that the radiometric method permits this relation to be investigated very simply.

We have already pointed out that the radiometric method of determining composition may be useful in cases where the reaction product has only a low color intensity, and even when it is colorless.

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* The pH of the buffer solution was controlled by means of a pH-meter.

** Centrifuging ensured good phase separation.

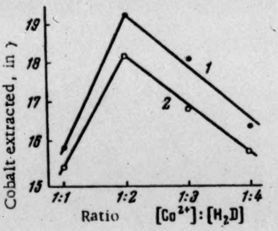

Fig. 6. Composition of Cobalt dithizonate; sum of components 2 μ mol/ 6 ml:

1) experiments carried out pH 7.6;

2) experiments carried out at pH 10

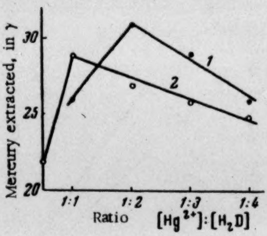

Fig. 7. Composition of mercury dithizonate; sum of components 0.2 μ mol/ 6 ml:

1) experiments carried out at pH 4.1;

2) experiments carried out at pH 9.8

TABLE 5

Composition of Cobalt Dithizonate

Content of components in μ mol/3 ml		Ratio $Co^{2+}:H_2D$	Specific activity in impulses/min. per 1γ Co^{2+}	pH of the medium		
Co^{2+}	H_2D			5.8	7.6	10
				Amount of Co^{2+} extracted in γ		
1	1	1:1	50	15.0	15.8	15.3
0.67	1.33	1:2		17.9	19.2	18.0
0.5	1.5	1:3		15.5	18.1	16.8
0.4	1.6	1:4		14.7	16.3	15.7
0.1	0.1	1:1	530	—	1.50	1.40
0.067	0.133	1:2		—	1.70	1.60
0.05	0.15	1:3		—	1.54	1.41
0.04	0.16	1:4		—	1.48	1.35

TABLE 6

Composition of Mercury Dithizonate.

Content of components in μ mol/3ml		Ratio Hg^{2+} : HeD	Specific activity in impulses/ min. per γ Hg^{2+}	pH of the medium					
Hg^{2+}	H_2D			0.9	1.8	4.1	5.8	7.6	9.8
				Amount of Hg^{2+} extracted in γ					
1.33	0.67	2:1 (1:0.5)	40	—	—	—	—	—	61
1	1	1:1		95	89	99	95	102	115
0.67	1.33	1:2		106	104	113	106	111	85
0.5	1.5	1:3		97	97	99	95	81	80
0.4	1.6	1:4		89	82	92	75	75	73
0.67	0.33	2:1 (1:0.5)	190	—	—	—	—	—	22
0.5	0.5	1:1		—	—	26	—	—	29
0.33	0.67	1:2		—	—	31	—	—	27
0.25	0.75	1:3		—	—	29	—	—	26
0.2	0.8	1:4		—	—	26	—	—	25

We have studied the composition of zinc hydroxyquinolate, which at low concentrations is extracted by an organic solvent to form a pale yellow solution. During determination of the composition of zinc hydroxyquinolate, the concentrations of the components were changed within the limits(1-0.1 μ mol/ml). As our tests

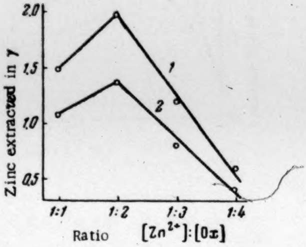

Fig. 8. Composition of zinc hydroxyquinolate. Sum of components 0.2 μ mol/6 ml:
1) experiments carried out at pH 7.6;
2) experiments carried out at pH 12.2.

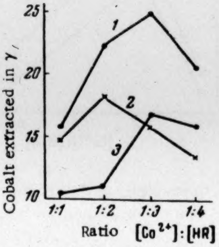

Fig. 9. Composition of cobalt α-nitroso-β-naphtholate. Sum of components 2 μ mol/6 ml:
1) experiments carried out at pH 7.6;
2) experiments carried out at pH 10.0;
3) experiments carried out at pH 5.8.

TABLE 7
Composition of Zinc Hydroxyquinolate

Content of components in μ mol/3 ml		Ratio of Zn^{2+} : hydroxyquinoline	Specific activity in impulses/min. per γ Zn^{2+}	pH of the medium	
				7.6	12.2
Zn^{2+}	Hydroxyquinoline			Zn extracted in γ	
1	1	1 : 1	75	19.2	20.8
0.67	1.33	1 : 2		30.2	32.2
0.5	1.5	1 : 3		21.6	25.4
0.4	1.6	1 : 4		10.5	17.3
0.1	0.1	1 : 1	160	1.1	1.5
0.067	0.133	1 : 2		1.4	2.0
0.05	0.15	1 : 3		0.8	1.2
0.04	0.16	1 : 4		0.4	0.6

Thus the composition of zinc hydroxyquinolate is expressed by the formula $Zn(Ox)_2$, which is in agreement with the results found by other methods. This example confirms the assumption regarding the possibility of carrying out radiometric determination of the composition of extraction products.

Conflicting results are given in the literature for the composition of cobalt α-nitroso-β-naphtholate. According to one source the nitrosonaphtholate of trivalent cobalt is formed [10, 11], while according to another the compound formed is a divalent cobalt derivative [12].

We studied the composition of cobalt α-nitroso-β-naphtholate in relation to the pH of the medium by the radiometric method. Experiments were carried out with solutions of the components containing $5 \cdot 10^{-3}$-$2 \cdot 10^{-4}$ mol/liter. Some of the experimental results are represented in Fig. 9.

It is interesting to note that the composition of cobalt α-nitroso-β-naphtholate depends on pH. Thus, in acid and weakly alkaline media, the composition of the compound can be expressed by the formula $Co(C_{10}H_6ONO)_3$, while in strongly alkaline media the appropriate formula is $Co(C_{10}H_6ONO)_2$.

The results obtained confirm our hypothesis regarding the possibility of using a radiometric method for determining composition.

SUMMARY

1. Calculations have been made of the amount of extracted reaction product in relation to a number of factors.

2. By using radioactive isotopes it is possible to study a number of questions arising during extraction from very dilute solutions; they can also be used for studying the extraction of pale or colorless reaction products.

3. Some of the conclusions reached are confirmed by radiometric determination of the composition of extracted zinc, mercury, and cobalt dithizonates and of extracted zinc hydroxyquinolate and cobalt α-nitroso-β-naphtholate.

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THE SOLUBILITY OF THE SELENITES OF CERTAIN METALS

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The solubility of metal selenites has not hiterto been determined. Meanwhile a knowledge of the solubility and solubility product of selenites is of importance for the analysis of materials containing selenium. We have determined the solubility of the selenites of mercury, nickel, cobalt, manganese, lead, iron, and cerium in dilute solutions of nitric, sulfuric, and hydrochloric acids respectively, and have calculated their solubility products. The selenites of the metals listed above were prepared from chemically pure reagents. Selenious acid and its sodium salt were prepared according to a method described by Klyuchnikov [1].

Mercurous Selenite. 0.1 N solutions of mercurous nitrate and sodium selenite were poured together in stoichiometric proportion in the cold. The precipitate was washed with water on a glass filter. Mercury was determined in the precipitate dried at 20° by titration with ammonium thiocyanate, while selenium was determined by weighing in the elemental form after precipitation with hydrazine. The ratio in g-ions of mercury and selenite was 2:1.02.

Nickel Selenite. On pouring together 0.1 N solutions of sodium selenite and nickel sulfate a light green colored precipitate was formed. Sodium selenite was 5% in excess of the theoretical amount. The precipitate was kept for 24 hours in the mother liquor, the water was removed by decantation after centrifuging, and the precipitate dried at 40°. Nickel was determined gravimetrically as the dimethylglyoximate, while selenium was weighed in the elemental form after precipitation with hydrazine. The ratio in g. ions of nickel to selenite was 1.02.

Cobalt Selenite. To 0.1 N cobalt nitrate was added 0.1 N sodium selenite at 50-60°. Excess sodium selenite was 3% of theory. The amorphous, violet precipitate was kept for a long time in the mother liquor. Washing was effected by decantation after centrifuging. The precipitate was dried at 40°. Cobalt was determined gravimetrically as the sulfate, while selenium was determined in the elemental form on a glass filter. The composition of the precipitate corresponded to a ratio (in g. ions) or cobalt to selenite of 1:0.99.

Selenite of Divalent Manganese. On pouring together 0.2 N solutions of manganese sulfate and sodium selenite, taken in stoichiometric proportion, a white bulky precipitate was formed. The solutions were heated to 50-70°. After standing for a long time in the mother liquor the precipitate changed into a crystalline form. Washing was carried out with water. The crystals which were dried at 40° were then analyzed. Manganese was determined gravimetrically as the sulfate, and selenium by weighing in the elemental form. The ratio in g. ions of manganese to selenite was 1.03.

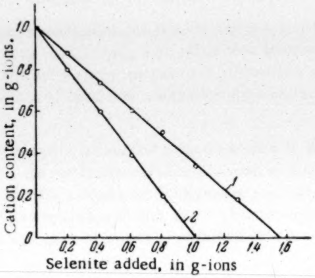
Lead Selenite. To a 0.2 N solution of lead acetate acidified with acetic acid was added 0.1 N sodium selenite in stoichiometric proportion at 50-60°. The white crystalline precipitate was washed with water and dried at 40°. Lead was determined gravimetrically as sulfate while selenium was determined gravimetrically in the elemental form. The ratio in g, ions of lead to selenite was 1.01.

Iron Selenite. To a 0.2 N solution of iron sulfate was added with stirring 0.1 N sodium selenite in an amount sufficient to form the neutral salt. The pH of the solution was 5-6. The precipitate was left in the mother liquor for 24 hours, it was washed by decantation after centrifuging, and dried at 40°. Iron was determined titrimetrically after reduction with zinc amalgam. Selenium was precipitated with hydrazine and weighed on a glass filter. The ratio of iron to selenite in terms of g. ions was 2:3.04.

Cerium Selenite. 0.1 N solutions of selenious acid and cerium selenite were poured together in stoichiometric proportion at 50°. The solution was neutralized with ammonia till it gave a weakly alkaline reaction to litmus. The precipitate was washed with water by decantation after centrifuging, and then dried at 40°. Cerium was determined gravimetrically as the dioxide, and selenium by weighing in the elemental form. The ratio in g. ions of cerium to selenite was 2:2.98.

Taking into account that the results of chemical analysis only enable one to have an idea of the average chemical composition of the precipitate, we determined the composition of the selenite precipitates during the precipitation process.

With this idea in mind we added various amounts of solution containing the selenite ion to equal amounts of standard solutions of the salts of mercury, nickel, cobalt, lead, and iron, the solution being agitated during addition. The selenite ion concentration was determined accurately. On addition of the reagents the corresponding selenite was precipitated; the residual content of cation was then determined in the liquid phase. It was shown in the course of these experiments that the composition of the precipitate did not change in the presence of excess selenite ion. As an example, we have given in the diagram the curves obtained during precipitation of the selenites of cobalt and iron. The amount of selenite ions added in g. ions is plotted along the abscissa while the residual amount of metal is plotted along the ordinate. The curves confirm the agreement between the composition of the precipitate and its formula.



Change in the cation content of the solution during formation of the precipitate.
1) Iron selenite; 2) cobalt selenite.

The solubility of the selenites was determined in dilute solutions of nitric, hydrochloric, and sulfuric acid. pH was measured on a MOSKIP pH-meter using a glass electrode. The accuracy with which pH was measured was ± 0.01 pH units. The pH meter was checked against standard buffer solutions prepared according to Britton [2]. The exact value of the pH of the buffer solutions was determined potentiometrically using the quinhydrone electrode. In order to get saturated solutions, the flasks containing the metal selenite and acid solution of known pH were placed in a thermostat. The temperature was kept constant to within ± 0.05°. The time taken to reach the saturated state was detemined in preliminary tests. It was found that shaking for 8 hours was sufficient to reach saturation. pH was determined on one part of the saturated solution, while the metal ion concentration of the solution was determined on another. Check tests showed that the composition of the solid phase did not change during attainment of the saturated solutions. Solid and liquid phases were separated by centrifuging. Mercury was determined by titration with 0.01 N ammonium thiocyanate, nickel was determined by weighing as its dimethylglyoximate, and cobalt determined gravimetrically as sulfate. Photometric methods were used for determining iron and manganese; divalent manganese was oxidized to the septivalent state by means of ammonium persulfate. Color intensity was measured on an FEK-M photoelectrocolorimeter. Lead was determined gravimetrically as the sulfate and cerium determined titrimetrically.

Results of duplicates agree reasonably well, Deviation from the mean did not exceed 5%.

Solubility product was calculated on the basis of a formula proposed by Babko for precipitates which are soluble in acids [3]. This method was used by Korenman for establishing the solubility products of the oxalates of a number of rare-earth elements [4]. The method used for calculation was checked by determining the solubility product of calcium oxalate and gave good results. Earlier, this method was used by Zharovsky for calculating the solubility product of phosphates [5]. The absence of data relating to activity coefficients meant that we were unable to calculate activity products for selenites. The concentration of the selenite ion which is necessary for calculating solubility products was determined from the values of the dissociation constants of selenious acid, hydrogen ion concentration, and metal ion concentration. The dissociation constants of selenious acid have been determined by a number of investigators. Britton and Robinson found $K_1 = 2.88 \cdot 10^{-3}$ and $K_2 = 0.95 \cdot 10^{-8}$ by potentiometric titration with a glass electrode at 18° [6]. Using potentiometric titration in conjuction with the quinhydrone electrode, German, Britton, and Robinson found the following values: $K_1 = 3.09 \cdot 10^{-3}$ and $K_2 = 0.89 \cdot 10^{-8}$ at 17° [7]. Willcox and Prideaux [8] found $K_1 = 4 \cdot 10^{-3}$ and $K_2 = 0.87 \cdot 10^{-8}$ by a photometric method at room temperature. In our work we have used the values of $K_1 = 4 \cdot 10^{-3}$ and $K_2 = 1 \cdot 10^{-8}$ found by Rumpf [9] who used a potentiometric method involving the glass electrode. The total concentration [S] of the acid which is the same as that of the precipitate is equal to:

$$[S] = [H_2SeO_3] + [HSeO_3^-] + [SeO_3^{2-}].$$

Substituting the values of the individual forms of the acid by the values $[H^+]$, K_1, K_2, we get

$$[S] = \frac{[H^+]^2}{K_1 K_2}[SeO_3^{2-}] + \frac{[H^+]}{K_2}[SeO_3^{2-}] + [SeO_3^{2-}] =$$

$$= \left[\frac{[H^+]^2 + K_1[H^+] + K_1K_2}{K_1K_2}\right] \cdot [SeO_3^{2-}].$$

Substituting $\frac{[H^+]^2 + K_1[H^+] + K_1K_2}{K_1 K_2} = \frac{1}{q}$, we get

$$[SeO_3^{2-}] = q\,[S]. \qquad (1)$$

The coefficient q only depends on hydrogen ion concentration. For convenience in using formula (1) we compiled Table 1 which contains the values of $-\log\ [SeO_3^{2-}]$ at $[S] = 1$ for various pH values. E.g., at pH = 1

$$[SeO_3^{2-}] = \frac{K_1 K_2}{K_1 K_2 + K_1[H^+] + [H^+]^2} = \frac{4 \cdot 10^{-11}}{4 \cdot 10^{-11} + 4 \cdot 10^{-4} + 10^{-2}} = 3.85 \cdot 10^{-9},$$

from which $-\log [SeO_3^{2-}] = 8.41$.

The total concentration of selenious acid was found from the concentration of metal ion in the saturated solution. For precipitates of the type $MeSeO_3$, $[S] = [Me^{2+}]$; for precipitates of the type Me_2--$(SeO_3)_3$ the total acid concentration $[S] = \frac{3}{2}[Me^{3+}]$, while for precipitates of the type Me_2SeO_3, $[S] = \frac{1}{2}[Me^+]$. The coefficient q was determined from the curve constructed on the basis of the figures given in Table 1; by multiplying it by the total concentration of selenious acid, the value of selenite ion concentration was determined. Results for the determination of solubility products are given in Tables 2-8.

The results given are the mean of two or more parallel experiments. The mean square error was determined by means of the formula given in the book by Batuner and Pozin [10].

TABLE 1

Values of $-\log\,[SeO_3^{2-}]$ for $[S] = 1$ and Various pH's

pH	$-\lg[SeO_3^{2-}]$	pH	$-\lg[SeO_3^{2-}]$	pH	$-\lg[SeO_3^{2-}]$
1	8.41	4	4.01	7	1.04
2	6.55	5	3.00	8	0.30
3	5.05	6	2.00	9	0.04

TABLE 2

Solubility and Solubility Product of Mercury Selenite (20°)

Solution	pH before shaking	pH of the saturated solution	Hg^{++} concentration, in g-ion/liter	$p\,[Hg^+]$	pq	$p\,[SeO_3^{2-}]$	$p\,[Hg^+]^2\,[SeO_3^{2-}]$
Sulfuric acid	2.69	2.72	$5.8 \cdot 10^{-5}$	4.24	5.49	10.05	18.53
	2.06	2.20	$1.3 \cdot 10^{-4}$	3.89	6.20	10.39	18.17
Nitric acid	2.95	3.05	$2.6 \cdot 10^{-5}$	4.58	5.03	9.92	19.08
	2.40	2.59	$7.2 \cdot 10^{-5}$	4.14	5.66	10.10	18.38
	2.08	2.22	$1.1 \cdot 10^{-4}$	3.96	6.18	10.44	18.36

Mean value $L_{p\,[Hg^+]^2 \cdot [SeO_3^{2-}]}$ . . . . . $(3.8 \pm 2.2) \cdot 10^{-19}$.

TABLE 3

Solubility and Solubility Product of Nickel Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Ni^{2+} concentration in g-ion/liter	$p\,[Ni^{2+}]$	pq	$p\,[SeO_3^{2-}]$	$p\,[Ni^{2+}]\,[SeO_3^{2-}]$
Nitric acid	2.41	7.12	$8.8 \cdot 10^{-3}$	2.06	0.91	2.97	5.03
	2.05	6.20	$2.6 \cdot 10^{-2}$	1.59	1.80	3.39	4.98
Sulfuric acid	2.74	7.68	$5.10 \cdot 10^{-3}$	2.29	0.50	2.79	5.08
	2.13	6.38	$2.1 \cdot 10^{-2}$	1.67	1.63	3.30	4.97
	2.08	6.26	$2.5 \cdot 10^{-2}$	1.60	1.72	3.32	4.92

Mean value $L_{p\,[Ni^{2+}] \cdot [SeO_3^{2-}]}$ . . . . $(1.0 \pm 0.1) \cdot 10^{-5}$.

TABLE 4

Solubility and Solubility Product of Cobalt Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Co^{2+} concentration in g-ion/liter	$p[Co^{2+}]$	pq	$p[SeO_3^{2-}]$	$p[Co^{2+}][SeO_3^{2-}]$
Nitric acid	2.41	5.69	$7.8 \cdot 10^{-3}$	2.11	2.30	4.41	6.52
	2.06	4.20	$3.5 \cdot 10^{-2}$	1.46	3.80	5.26	6.72
Sulfuric acid	2.74	6.39	$2.0 \cdot 10^{-3}$	2.70	1.60	4.30	7.00
	2.13	4.30	$2.1 \cdot 10^{-2}$	1.68	3.70	5.38	7.06
	2.08	4.25	$2.7 \cdot 10^{-2}$	1.57	3.75	5.32	6.89

Mean value $L_p [Co^{2+}] [SeO_3^{2-}] \ldots (1.6 \pm 0.8) \cdot 10^{-7}$.

TABLE 5

Solubility and Solubility Product of Manganese Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Mn^{2+} concentration in g-ion/liter	$p[Mn^{2+}]$	pq	$p[SeO_3^{2-}]$	$p[Mn^{2+}][SeO_3^{2-}]$
Sulfuric acid	2.69	6.07	$3.1 \cdot 10^{-3}$	2.51	1.94	4.45	6.96
	2.06	4.35	$2.8 \cdot 10^{-2}$	1.55	3.63	5.18	6.73
Hydrochloric acid	2.79	6.24	$2.2 \cdot 10^{-3}$	2.66	1.77	4.43	7.09
	2.41	5.37	$6.8 \cdot 10^{-3}$	2.17	2.60	4.77	6.94
	2.05	4.42	$2.1 \cdot 10^{-2}$	1.68	3.58	5.26	6.94

Mean value $L_p [Mn^{2+}] [SeO_3^{2-}] \ldots (1.2 \pm 0.4) \cdot 10^{-7}$.

TABLE 6

Solubility and Solubility Product of Lead Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Pb^{2+} concentration in g-ion/liter	$p[Pb^{2+}]$	pq	$p[SeO_3^{2-}]$	$p[Pb^{2+}][SeO_3^{2-}]$
Hydrochloric acid	2.05	2.21	$2.9 \cdot 10^{-3}$	2.54	6.20	8.74	11.28
	2.79	3.12	$4.2 \cdot 10^{-4}$	3.38	4.95	8.33	11.71
Nitric acid	2.95	3.38	$3.1 \cdot 10^{-4}$	3.47	4.66	8.13	11.60
	2.40	2.85	$8.3 \cdot 10^{-4}$	3.08	5.25	8.33	11.41
	2.08	2.25	$2.3 \cdot 10^{-3}$	2.64	6.15	8.79	11.43

Mean value $L_p [Pb^{2+}] [SeO_3^{2-}] \ldots (3.4 \pm 1.3) \cdot 10^{-12}$.

TABLE 7

Solubility and Solubility Product of Iron Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Fe^{3+} concentration in g-ion/liter	$p[Fe^{3+}]$	pq	$p[SeO_3^{2-}]$	$p[Fe^{3+}]^2 \cdot [SeO_3^{2-}]^3$
Nitric acid	2.41 2.05	2.68 2.12	$1.1 \cdot 10^{-3}$ $3.4 \cdot 10^{-3}$	2.96 2.47	5.50 6.33	8.28 8.61	30.76 30.77
Sulfuric acid	2.74 2.13 2.08	2.97 2.22 2.17	$8.2 \cdot 10^{-4}$ $2.6 \cdot 10^{-3}$ $2.9 \cdot 10^{-3}$	3.09 2.58 2.54	5.13 6.20 6.27	8.04 8.61 8.63	30.30 30.99 30.97

Mean value $L_p\,[Fe^{3+}]^2\,[SeO_3^{2-}]^3 \ldots (2.0 \pm 1.7) \cdot 10^{-31}$.

TABLE 8

Solubility and Solubility Product of Cerium Selenite (20°)

Solution	pH before shaking	pH of saturated solution	Ce^{3+} concentration in g-ion/liter	$p[Ce^{3+}]$	pq	$p[SeO_3^{2-}]$	$p[Ce^{3+}]^2\,[SeO_3^{2-}]^3$
Nitric acid	2.45 2.12	3.99 3.43	$2.6 \cdot 10^{-3}$ $5.9 \cdot 10^{-3}$	2.58 2.23	4.00 4.60	6.41 6.65	24.39 24.41
Sulfuric acid	2.31 2.03	3.71 3.22	$3.8 \cdot 10^{-3}$ $7.6 \cdot 10^{-3}$	2.42 2.12	4.30 4.85	6.54 6.79	24.43 24.61

Mean value $L_p\,[Ce^{3+}]^2[SeO_3^{2-}]^3 \ldots (3.7 \pm 0.3) \cdot 10^{-25}$.

SUMMARY

The solubility products of the following selenites were determined at 20°:

$$L_{p[Hg^+]^2 \cdot [SeO_3^{2-}]} = (3.8 \pm 22) \cdot 10^{-19}$$

$$L_{p[Ni^{2+}] \cdot [SeO_3^{2-}]} = (1 \pm 0.1) \cdot 10^{-5}$$

$$L_{p[Co] \cdot [SeO_3^{2-}]} = (1.6 \pm 0.8) \cdot 10^{-7}$$

$$L_{p[Mn^{2+}] \cdot [SeO_3^{2-}]} = (1.2 \pm 0.4) \cdot 10^{-7}$$

$$L_{p[Pb^{2+}] \cdot [SeO_3^{2-}]} = (3.4 \pm 1.3) \cdot 10^{-12}$$

$$L_{p[Fe^{3+}]^2 \cdot [SeO_3^{2-}]^3} = (2 \pm 1.7) \cdot 10^{-31}$$

$$L_{p[Ce^{3+}]^2 \cdot [SeO_3^{2-}]^3} = (3.7 \pm 0.3) \cdot 10^{-20}$$

On the basis of this data graphs have been plotted.

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THE EFFECT OF THE MOISTURE CONTENT OF SILICA GEL ON THE CHROMATOGRAPHIC SEPARATION OF GASES

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One of the principal advantages of adsorption methods of analysis as compared with those based on distillation is the possibility of varying the adsorbent so that differences in adsorbability can be increased [1]. There is a considerable number of various adsorbents which can be used for separating and analyzing gas mixtures. Further, depending on the method of preparation, it is possible to alter the adsorbing properties of a given type of adsorbent over wide ranges [2]. Chromatography [3,4] consists of the simultaneous action on the adsorbed mixture of a solvent and a moving temperature field; this ensure a high degree of resolution of complex gas mixtures. Usually chromathermograph No. 5 is used for individual determination of saturated and unsaturated hydrocarbons, for analyzing industrial gases, cracking gases, and gases from the pyrolysis of petroleum. Silica gel is used as the adsorbent [5].

The silica gel turned out by Russian industry is not sufficiently standard in quality, and accordingly a series of analyses does not yield identical results during analysis on silica gel of the same type and particle size but produced at different times. This is particularly true of the separation of saturates and unsaturates, and especially of the separation of mixtures of ethane and ethylene and of propylene, butane, and butylene. Further, on some types of silica gel, partial polymerization of unsaturated hydrocarbons – particularly isobutylene – occurs. In order to eliminate these drawbacks it is necessary to develop a technique which will allow the properties of the adsorbent to be varied within wide limits. In the present article a description is given of results obtained during a study of the properties of the adsorbent, and of its standardization, and of the effect of addition of water to the silica gel on the completeness of separation of saturated and unsaturated hydrocarbons.

Let us consider methods of solving the problems confronting us, viz: suppressing polymerization on silica gel, and looking for ways of varying the adsorption properties of the silica gel continuously. Both problems are of essential importance for analyzing mixtures containing unsaturated hydrocarbons. We shall dwell briefly therefore on the mechanism of adsorption of unsaturated hydrocarbons. The values of the molecular adsorption for unsaturated and saturated hydrocarbons with an equal number of carbon atoms differ appreciably from one another. This is evident from results on the adsorbability of these hydrocarbons on activated charcoal.

If one makes use of known semiempirical relations, then unsaturated hydrocarbons, which in the overwhelming majority of cases have the lower boiling points, should be adsorbed better than the saturates. It is obvious that the specific adsorption of unsaturated hydrocarbons has the character of activated adsorption. It is highly probable that this process is realized as a result of acceptor-donor bonds between the π-electrons of ethylene and the hydrogen ions which are always present on silica gel. It is known [6] that the catalytic activity of the gel is related to the presence of hydrogen ions. It is obvious that if acceptor-donor bonds play a significant role, irreversible adsorption of unsaturated hydrocarbons is possible. Thus the problem arises of weakening and regulating this specific interaction.

The acidity of silica gel can be decreased considerably by adding alkali; thereby the catalytic activity is also decreased. Nevertheless, if this is done there is danger of suppressing adsorption capacity also.

Water should be a milder agent. The effect of the moisture content of the adsorbent on its sorption properties has been studied repeatedly [7-9]. A molecule of water which is adsorbed in an orientated state, thereby forming hydrated envelope round the hydrogen ion, may lead to a decrease in the interaction being studied to such an extent that the catalytic effect disappears, while the specific adsorption of unsaturated hydrocarbons is preserved. It can also be postulated that the molecule of water, on account of its small dimensions, blocks the more active centers of the silica gel on which the catalytic processes leading to polymerization of unsaturated hydrocarbons occur.

Silica gel is obtained by the interaction of technical liquid glass and technical sulfuric acid. Depending on the pH of the wash liquor, fine or coarse pore silica gel is obtained. Drying is usually carried out by means of flue gas at 450°. Silica gel prepared in this way is not standard and contains various amounts of HCl, H_2SO_4 , and other impurities.

In our experiments we used activated fine pore silica gel marks ASM and MSM, and coarse pore silica gel marks ShSK and KGSG, all of Russian manufacture. It is known that the amount of hydroxyl groups which are found on the surface of the silica gel, and determine its nature, depend on the method of preparing the adsorbent [10,11] , and on its additional activation before analysis. In our experiments a standard method of treating the silica gel was adopted.

The silica gel which was dried at 200° was sieved and the fractions with particle size 0.25-0.5 mm repeatedly dried at 200° to constant weight. The silica gel was then calcined in an electric oven at 1100° for 16 hours in order to determine the absolute amount of structural water. The percentages of water found in the MSM, ASM, ShSK, and KGSG silica gels were respectively 3.18, 4.71, 4.29, and 4.40%. In addition the contents of SO_4^{2-} and Cl^- ions of the wash liquor were also determined.

Ethylene, propylene, and butylene were prepared by dehydrating the corresponding alcohols in an oven, using aluminum oxide as catalyst. The saturated hydrocarbons were prepared by hydrogenation of the corresponding hydrocarbons over nickel, the reduction being carried out in a stream of hydrogen; separation of hydrocarbons from excess hydrogen was effected by condensing them in liquid nitrogen. Unsaturated hydrocarbons were removed by absorption in sulfuric acid and bromine water. The purity of the fractions was checked by determination of the carbon number, and on chromathermograph No. 4.

The technique used was to place a mixture of materials at known concentrations on a column filled with adsorbent, followed by developement of the chromatogram by the simultaneous action of a stream of air purified from water vapor and acid gases, and a moving temperature field obtained by means of an electric oven, inside which there was a constant temperature gradient.

Measurements of the concentrations after passing through the absorbent layer were carried out continuously on a thermochemical gas analyzer, or on an apparatus based on measurement of the thermal conductivityof the gases.

The characteristic temperature at which the components separate out was measured with an accuracy of up to 1°, using a copper-constantan thermocouple placed in the top of the silica gel layer.

In order to find the capacity of the adsorbent, the value of its retention volume by the frontal method was determined using the equation

$$a_0 = \Phi_0(C) = V_0 C. \tag{1}$$

Here C is the concentration of the material in solution; V_0 the volume of the solution which must be passed through the adsorbent until the material, at a given concentration, appears beyond the adsorbent.

The heat of adsorption Q for propylene and butane on the silica gel was calculated from the characteristic equation of chromathermography [12]

$$T_{\mathrm{char}} = -\frac{Q}{R \ln A \frac{w}{\alpha}}. \tag{2}$$

Here R is the gas constant; A is the adsorption constant; w the rate at which the oven is moved; and α is the linear flow rate.

On placing a definite amount of material on the adsorbent and changing the value of α and w, the temperature at the maximum of the elution curve was measured. The accuracy of determination amounts to 1%. The completeness of desorption of saturated and unsaturated hydrocarbons is determined by calculating the areas of the elution curves. First a certain amount of material was introduced into an empty tube and eluted with air. By carrying out continuous measurement of concentration with time by means of a low inertia apparatus, an elution curve was obtained. Next the same amount of material was placed on the adsorbent and developed with air. When the areas of the elution curves obtained during passage of gas through the empty tube and through the adsorbent coincided, it could be assumed that complete desorption of the material from the adsorbent had been achieved.

When silica gel was used, water vapor was removed from the test mixture, and the air passed through columns filled with calcium chloride and phosphorus pentoxide. When moist silica gel was used, the air was saturated beforehand with water vapor to a concentration equal to the equilibrium moisture content of the silica gel.

It was of primary importance to find an explanation for the polymerization of unsaturated hydrocarbons on silica gel.

Elution curves were taken for propylene and butylene on dry, unwashed silica gel Mark ASM, on silica gel Mark ASM washed free from H_2SO_4 and HCl, on silica gel Marks ASM, KGSG, ShSK and MSM to which had been added 5% water by weight, and also on silica gel to which KOH had been added. It was found that on unwashed silica gel Mark ASM, irreversible adsorption of propylene and butylene occurs.

Desorption of propylene amounted to only 15.5% while for butylene the value was 11%. When the same silica gel was used after being washed free from H_2SO_4 and HCl, and conditions were identical to those used before, desorption of unsaturated hydrocarbons was quantitative. Addition of water in amounts of 4-5% on the weight of the silica gel also ensured complete desorption. Addition of potassium hydroxide in amounts of 0.5 and 3% gave complete desorption of unsaturated hydrocarbons on silica gel. Addition to washed silica gel of H_2SO_4 in an amount equal to 0.1% of the silica gel led to incomplete desorption; propylene was only desorbed to the extent of 44.6%, and only 17.7% of butylene desorbed; addition of 5% HCl also led to incomplete desorption of the unsaturated hydrocarbons.

Thus, irreversible adsorption of unsaturated hydrocarbons on silica gel is caused mainly by the presence of sulfuric, and partially by hydrochloric acid. Neutralizing with KOH, or washing the silica gel free of the acids mentioned, lead to complete desorption of unsaturated gaseous hydrocarbons.

Results of a study of completeness of desorption of unsaturated hydrocarbons are given in Table 1.

The use of dry silica gel, preliminarily washed free of acids (H_2SO_4 and HCl) did not ensure separation of saturated and unsaturated hydrocarbons. The most difficult problem is separation of mixtures containing ethane, ethylene, propylene, butane, and butylene.

On using dry silica gel, ethane and ethylene could be separated quite well, but propylene and butane are not separated. The heat of adsorption of propylene and butane on silica gel Mark ShSK at a concentration of 3.6% was found to be 6900 calories/mole, while on Mark ASM the value found was 8000 calories/mole.

In Fig. 1* are given elution curves for mixtures of hydrocarbons on silica gel Marks MSM, ASM, and KGSG, at two temperatures. The amount of air used for elution is plotted along the abscissa while instrument readings in arbitrary units are plotted on the ordinate.

For α = 100 cm/min, w = 2.5 cm/min and a maximum oven temperature of 90°, good separation was achieved for hydrogen, methane, ethane, ethylene, propane, and propylene. There was hardly any desorption of butane and butylene at this temperature, but at a maximum oven temperature of 150° they were completely desorbed. Propylene and butylene were not separated. Dry silica gel Mark MSM (1951 production) proved the exception; using this material, mixtures of ethane, ethylene, propylene, butane, and butylene were separated.

Addition of alkali did not lead to an improvement in separation of propylene and butane. On adding 3% KOH the sorption capacity of siliga gel ASM decreased sharply. On adding 1.5% KOH the heat of adsorption of propylene and butane decreased from 8000 to 6000 calories/mole. It is obvious that addition of alkali to silica gel is not expedient.

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* In Figs. 1-3 the volume of air used for elution is given in cm^3.

A study was also made of the effect of additions of various amounts of water to silica gel Marks MSM, ASM, ShSK, and KCSG on the extent of separation of mixtures of hydrogen, methane, ethane, ethylene, propane, propylene, butane, butylene, and air.

Results of this study are represented in Figs. 2 and 3 and in Table 2.

It is evident from Table 2 that with increasing moisture content of the silica gel, the time required for developing individual hydrocarbons decreases. Under these conditions, development time differs for the various components.

Hydrogen is hardly adsorbed at all; consequently changes in the moisture content of silica gel have little influence on the development time of hydrogen. The effect of the moisture content of the silica gel on the retention volume is most marked in the case of ethylene. On adding 1% of water, the retention volume for ethylene on silica gel decreased by 35 - 40%, while on addition of 5% of moisture the retention volume decreased 3-4 times . Propane, at a low moisture content of the silica gel, moved forward at the rate of the oven in its temperature zone, and its retention volume changed relatively little. Starting at 2% moisture content of the silica gel, the propane moved with the oven and its retention volume decreased sharply.

Propylene, butane, and butylene moved in their temperature zones, and accordingly changed their position to a relatively small extent on increasing the moisture content of the silica gel. Nevertheless, addition of water showed a stronger effect on propylene and butylene than on butane. This is explained by the fact that on moist silica gel propylene is separated from butane and butylene, while butylene and butane do not separate so well as on dry silica gel. Thus addition of water to silica gel depressed the capacity of the silica gel for unsaturated hydrocarbons to a greater extent than for saturated hydrocarbons, which can be related to activated adsorption of unsaturated hydrocarbons on silica gel. The most active silica gel tested was activated fine pore ASM silica gel.

TABLE 1

	Amount taken in mm^2	Amount found in mm^2	Desorption in %
Silica gel Mark ASM dried at 200°			
Propylene	800	140	17.5
Butylene	1480	163	11.0
Silica gel Mark ASM washed, dry			
Propylene	700	700	100
Butylene	1015	930	91.6
Silica gel Mark ASM, dry, + 5% H_2O			
Propylene	340	338	99.93
Butylene	1000	990	99.0
Silica gel Mark ASM + 0.5% KOH			
Propylene	110	110	100
Butylene	—	—	—
Silica gel Mark ASM, washed, +1,65% HCl			
Propylene	750	550	73
Butylene	1015	670	66
Silica gel Mark ASM,washed +5% HCl			
Propylene	750	350	47
Butylene	1015	540	51
Silica gel Mark ASM, washed, +0,1% H_2SO_4			
Propylene	640	285	44.6
Butylene	850	150	17.7
Silica gel Mark AS M, washed +0,5% H_2SO_4			
	640	30	4.7
	850	65	7.7

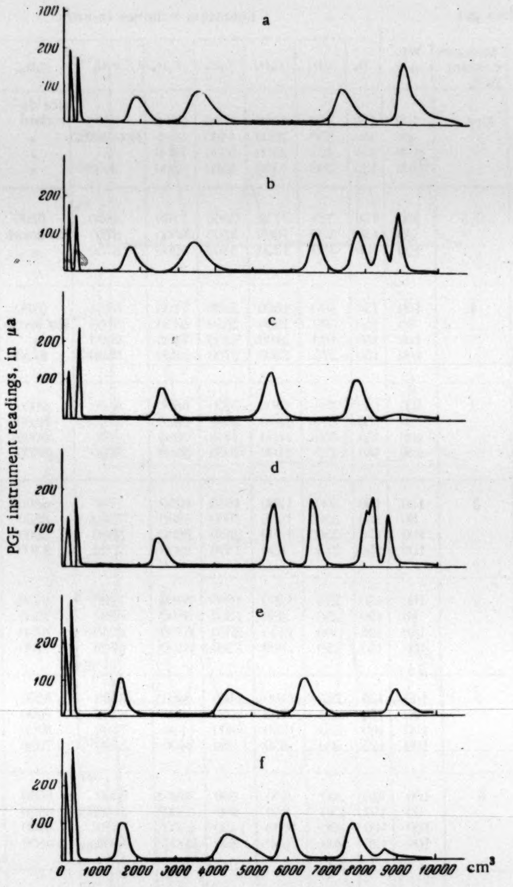

Fig. 1. Elution curves for mixtures of: hydrogen, methane, ethane, ethylene, propane, propylene, butane, butylene on dry silica gel of different marks:
a) MSM t_{max} = 90°; b) MSM t_{max} =150°; c) ASM t_{max} = = 90°; d) ASM t_{max} = 150°; e) KGSG t_{max} = 90°; f) KGSG t_{max} = 150°.

TABLE 2

Silica gel			Retention volumes in cm³							
Mark	Moisture content in %	Wt. in g	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8
MSM	Dry	100	150	350	1900	3500	7400	9100	Not desorbed	Not desorbed
ShSK		90	150	350	2000	4400	6900	Not desorb.	»	»
ASM		100	150	425	2600	5550	7900	»	»	»
KGSG		100	125	300	1550	4500	6500	9000	»	»
MSM	0,5	100	150	325	1750	3000	7100	8800	9200	»
ShSK		90	150	350	1600	3200	6600	8700	Not desorb.	»
KGSG		100	150	300	1350	3100	6000	8750	»	»
MSM	1	100	150	300	1600	2400	7100	8750	9200	»
ShSK		90	150	300	1500	2850	6450	8700	Not desorb.	»
ASM		100	150	400	2100	4100	7350	9000	»	»
KGSG		100	150	275	1300	2700	5800	8500	8750	»
MSM	2	100	150	300	1600	2400	6800	8500	9000	»
ShSK		90	150	250	1200	2000	6050	8000	8800	»
ASM		100	150	350	1850	3400	7000	8650	9000	»
KGSG		100	150	275	1100	2050	5300	8000	8600	»
MSM	3	100	150	300	1200	1650	6250	7700	8800	»
ShSK		90	150	250	1000	1600	4800	7300	8550	9150
ASM		100	150	350	1600	2600	6600	8600	9000	Not desorb.
KGSG		100	150	275	850	1400	3800	7050	8300	9100
MSM	4	100	150	275	1200	1600	5900	7200	8450	8800
ShSK		90	150	250	850	1300	3600	6800	7900	8950
ASM		100	125	300	1450	2300	6300	8250	8750	Not desorb.
KGSG		100	150	250	800	1200	3200	6700	7700	8750
MSM	5	100	125	225	1100	1100	4400	6400	8200	8600
ShSK		90	150	250	700	1050	3000	6300	7000	8800
ASM		100	100	250	1200	1800	5700	7700	8700	9150
KGSG		100	125	200	650	950	2400	5700	7050	8650
MSM	6	100	125	200	900	900	3600	6000	8000	8550
ShSK		90	150	250	650	900	2300	5100	6850	8600
ASM		100	100	250	1000	1450	4500	7050	8400	8950
KGSG		100	125	200	550	800	2000	4700	6500	8300
MSM	7	100	125	175	800	800	3100	5900	7700	8600
ShSK		100	100	250	900	1300	3800	6700	8100	8900
KGSG		100	125	200	475	650	1550	3250	5600	7700
MSM	8	100	125	175	750	750	2800	5200	7100	8300
ShSK		90	125	200	450	600	1300	2750	4850	7500
ASM		100	100	250	750	1050	3000	6000	7450	8650
KGSG		100	125	175	400	525	1150	2300	3800	7000

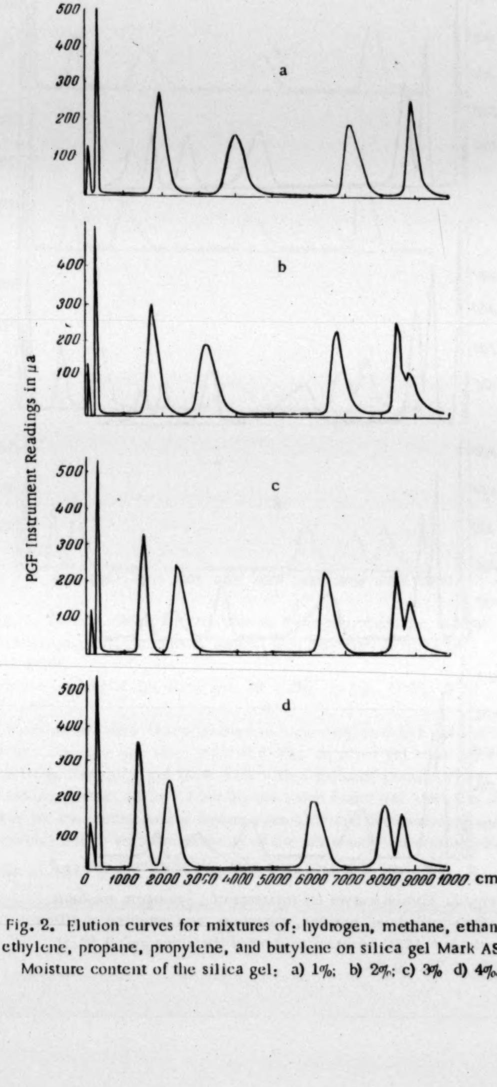

Fig. 2. Elution curves for mixtures of: hydrogen, methane, ethane, ethylene, propane, propylene, and butylene on silica gel Mark ASM. Moisture content of the silica gel: a) 1%; b) 2%; c) 3% d) 4%.

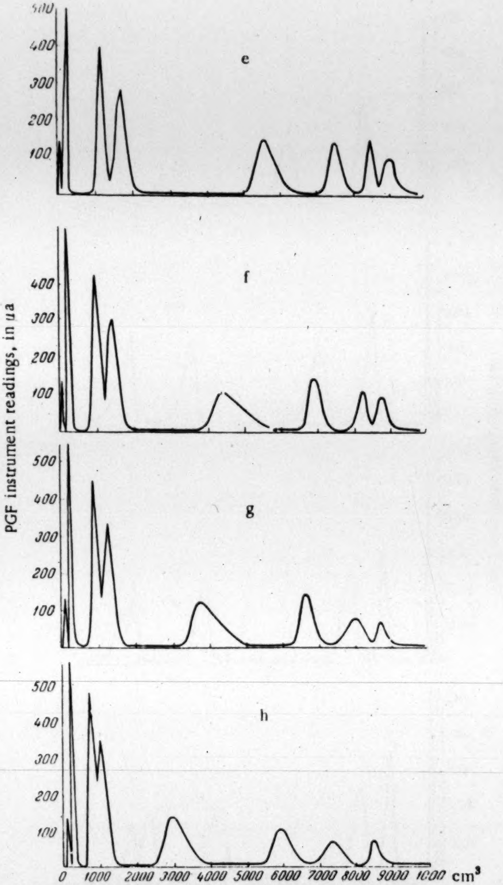

Fig. 2. Elution curves for mixtures of : hydrogen, methane, ethane, ethylene, propane, propylene, and butylene on silica gel Mark ASM. Moisture content of the silica gel: e) 5%; f) 6%; g) 7%; h) 8%.

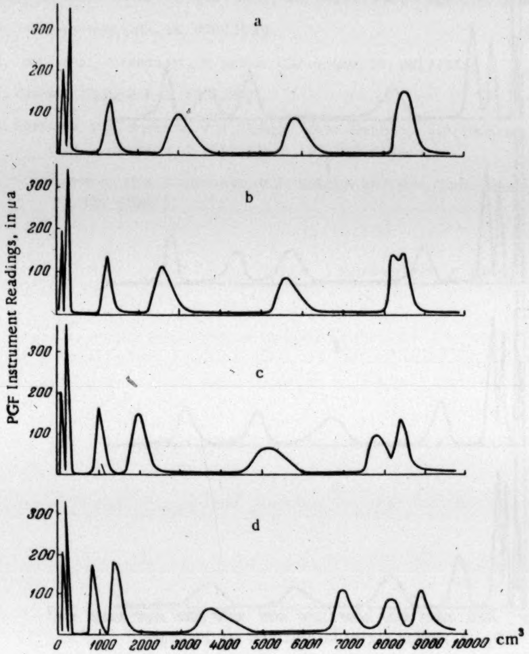

Fig. 3. Elution curves for mixtures of: hydrogen, methane, ethane, ethylene, propane, propylene, butane, and butylene on silica gel Mark KGSG.
Moisture content of the silica gel: a) 0.5%; b) 1%; c) 2%; d) 3%.

The results of these studies show that quantitative separation on silica gel Mark ASM is achieved at a moisture content of 5-6%, on silica gel Mark ShSK at 4-5%, on silica gel Mark MSM at 3-4%, and on silica gel Mark KGSG at 4-5%. On silica gel Mark ASM with a moisture content of 5%, the heat of adsorption for propylene was 6600 calories/ mole, while for butane the value found was 7400; on Mark ShSK silica gel with a moisture content of 5% the corresponding figures were 5100 and 6500 calories/ mole. Thus addition of water to the silica gel enables one to vary the capacity of the adsorbent to a considerable extent.

The authors wish to thank A.A. Zhukhovitsky for valuable help and for the interest he showed in the work.

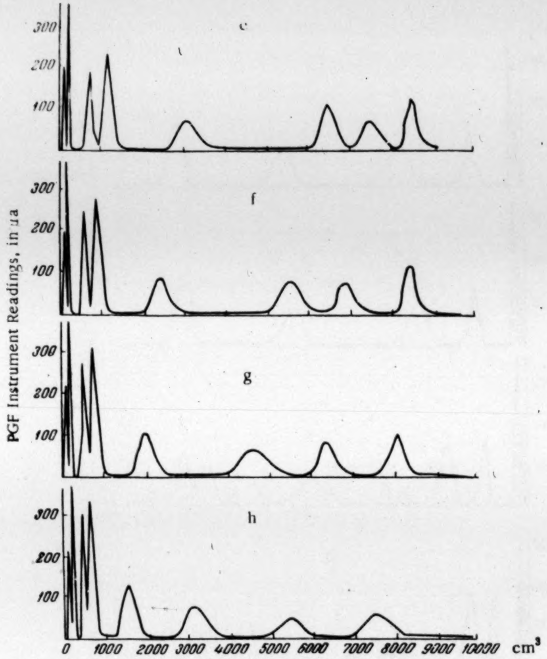

Fig. 3. Elution curves for mixtures of: hydrogen, methane, ethane, ethylene, propane, propylene, butane, and butylene on silica gel Mark KGSG. Moisture content: e) 4%; f) 5%; g) 6%; h) 7%.

SUMMARY

Adsorption of unsaturated hydrocarbons on silica gel seems to bear the character of activated adsorption. The irreversible adsorption of unsaturated hydrocarbons on silica gel is mainly the result of the presence of sulfuric acid in the silica gel. By changing the amount of water in the silica gel, it is possible to regulate the process of activated adsorption and to vary the capacity of the adsorbent.

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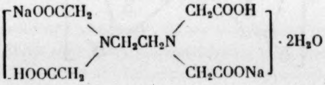
APPLICATION OF COMPLEXONE III FOR THE CHROMATOGRAPHIC SEPARATION OF RUBIDIUM AND CESIUM

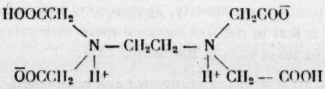
A.P. Smirnov-Averin, G.B. Kostarev, and N.N. Krot

In recent years a considerable amount of attention has been given in the literature to compounds called "complexones". This name was suggested in 1945 by Schwarzenbach for compounds whose molecules contain at least one atom of nitrogen to which is attached at least two carboxyl groups – usually in the form of radicals $-CH_2COOH$. The most important and most studied complexones are ethylenediaminetetracetic acid [1], and its disodium salt which possesses two molecules of water – Complexone III:



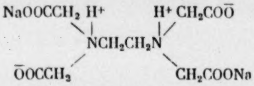
Ethylenediaminetetracetic acid $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$ is often called "Complexone II" in the literature and is designated by the formula H_4Y. Of other complexones, nitriltriacetic acid (Complexone I) [2], uramyldiacetic acid [3], and 1,2-diaminecyclohexanetetracetic acid [4], have also been fairly widely used (mainly in analytical chemistry). Complexone III is a white crystalline powder which is readily soluble in water and insoluble in the usual organic solvents. At 21° 100 ml of a saturated aqueous solution of Complexone III contains 11.1 g. of the latter [5]. On acidifying aqueous solutions, a precipitate of ethylenediaminetetracetic acid settles out which is only sparingly soluble in water. Precipitation is complete at a pH ~ 2 [6]. Complexone III is not hygroscopic and is stable on storage both in the dry state and in solution [7,8]. By precipitation from aqueous solution by addition of alcohol it is possible to get it in a very pure form [5].

Complexone III is a salt of the rather weak acid ethylenediaminetetracetic acid. The pK values for its four dissociation stages as determined from its neutralization curves have been found to be equal to (1): $pK_1 = 2.0$; $pK_2 = 2.7$; $pK_3 = 6.2$ and $pK_4 = 10.3$ (at a temperature of 20° and an ionic strength for the solution of 0.1). The sharp difference between pK_1 and pK_2 on the one hand, and pK_3 and pK_4 on the other, is explained by a difference in the position of the protons in the molecule of ethylenediaminetetracetic acid:



The protons on the carboxyl groups have a more acid character, i. e. they are split off comparatively easily (pK_1 and pK_2). The two other protons linked to the nitrogen atom are much more difficult to split off (pK_3 and pK_4).

A similar doublet-like structure is also characteristic of Complexone III:

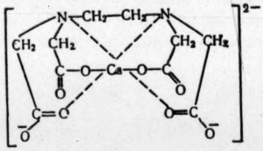


Accordingly, in aqueous solution Complexone III dissociates mainly according to the scheme

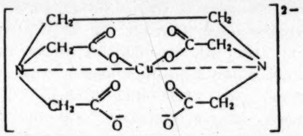
$$Na_2HY \rightleftarrows 2Na^+ + H_2Y^{2-}.$$

Complexone III is exactly analogous to ethylenediaminetetracetic acid as a complexing agent; it is characterized above all by the fact that it has so many applications. Complex compounds formed between it and the following elements have been studied: alkaline-earths, rare earths, Mg, Zn, Ni, Cu, Cd, Pb, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Al, Cr^{3+}, In^{3+}, V^{2+}, VO^{2+}, V^{3+}, Bi^{3+}, Sc, Li, Na, etc. Of the elements studied the ones which show the least tendency to form complexes are Tl^+, Be^{2+}, ions of the alkali metals, and some other elements.

The compounds formed can be assigned to the class of inner complex salts. As an example we have given below the structural formula of the compound formed between Complexone III and Ca^{2+} [9]:



Here the calcium ion has a coordination number of 6. Complexone III forms the following type of compound with ions which have a coordination number 4, such as copper ions [10]:



The stability of these compounds, however, cannot be explained purely by their cyclic structure [11] One must also bear in mind the large charge of the anion of ethylenediaminetetracetic acid and its high coordination capacity. Schwarzenbach has called this effect of an increase in stability of complex compounds as a result of an increase in the coordination capacity of the substituent the "chelate effect" [12]. This effect can be explained by a more significant increase in entropy during the process of complex formation of metal ions with substituents with a high coordination capacity, as compared with substituents with a low coordination number . What it really reduces to is that in the first instance more molecules of water are freed from the hydrated envelope of the ion per substituent than in the second case.

Compounds of Complexone III with many elements have been studied quantitatively [13-19]. In Table 1 is given a summary of published results on the stability of complexes formed with certain elements. The values adduced for the logarithm of the stability constants of the complexes were obtained at 20° in a solution with ionic strength of 0.1.

It is evident from these results that the stability of the complex compounds formed, as a rule, increases with the increase in the charge of the ion complexed and decreases with increasing ionic radius.

TABLE 1

$K = [MeY]/[Me][Y]$

Complex	log K	Reference	Complex	log K	Reference
$[HY]^{3-}$	10.22	[14]	$[GdY]^-$	17.37	[14]
$[LiY]^{3-}$	2.79	[14]	$[TbY]^-$	17.93	[14]
$[CuY]^{2-}$	18.80	[14]	$[DuY]^-$	18.30	[14]
$[MgY]^{2-}$	8.69	[14]	$[HoY]^-$	18.74	[14]
$[CaY]^{2-}$	10.96	[14]	$[ErY]^-$	18.85	[14]
$[SrY]^{2-}$	8.63	[14]	$[TmY]^-$	19.32	[14]
$[BaY]^{2-}$	7.76	[14]	$[YbY]^-$	19.51	[14]
$[ZnY]^{2-}$	16.50	[14]	$[LuY]^-$	19.83	[14]
$[CdY]^{2-}$	16.46	[14]	$[PbY]^{2-}$	18.04	[14]
$[HgY]^{2-}$	21.80	[14]	$[TiOY]^{2-}$	17.3	[19]
$[AlY]^-$	16.13	[14]	$[TiY]^-$	21.3	[19]
$[GaY]^-$	20.27	[14]	$[TiY]$	19.4	[19]
$[InY]$	24.95	[14]	$[ThY]$	23.2	[14]
$[ScY]$	23.1	[14]	$[VY]^{2-}$	12.7	[16]
$[YY]$	18.08	[18]	$[VY]^-$	25.9	[16]
$[LaY]^-$	15.50	[14]	$[VOY]^{2-}$	18.77	[16]
$[CeY]^-$	15.98	[14]	$[MnY]^{2-}$	13.47	[13]
$[NdY]^-$	16.61	[14]	$[FeY]^{2-}$	14.4	[17]
$[PrY]^-$	16.40	[14]	$[FeY]^-$	25.1	[15]
$[SmY]^-$	17.14	[14]	$[NiY]^{2-}$	18.62	[14]
$[EuY]^-$	17.35	[14]	$[CoY]^{2-}$	16.31	[14]

The complexing properties of Complexone III are widely used in industry [20], and particularly in analytical chemistry [21, 22]. Much work has also been devoted to studies of solutions of Complexone III as eluents for the chromatographic separation of elements similar in properties. Thus a series of papers by American authors [23-25] described the use of Complexone III solutions for the chromatographic separation of rare earths. It was shown in the course of this work that Complexone III is a more efficient eluent that citric acid, since differences in the stability of the complex compounds formed between rare earths and Complexone III are greater than in the case when citric acid is used; further, Complexone III can be used in more concentrated solutions than citric acid, as a result of which the rate at which the rare earths can be separated is speeded up several times.

Complexone III nevertheless does have some disadvantages: it is difficult to work with this compound at low pH since ethylenediaminetetracetic acid separates out and blocks the column.

The complexes formed between rare earths and Complexone III exhibit considerable stability. Consequently the complexes formed at the top of the column pass through the whole layer of adsorbent without breaking down, and the lanthanides are not separated. This difficulty has been overcome by using columns in the Fe^{3+} form [24], or in the Cu^{2+} form [25]. When this is done, the Fe^{3+} and Cu^{2+} ions displace the ions of the rare earths from their complexes and ensure their repeated sorption and desorption, as a result of which they can be separated.

The use of Complexone III for the chromatographic separation of strontium and barium on Dowex-50 has also been described [26]. In this case the eluent used was a 0.01 M solution of Complexone III with a pH of 7.4, the elution rate being 1.3 ml/cm^2/minute.

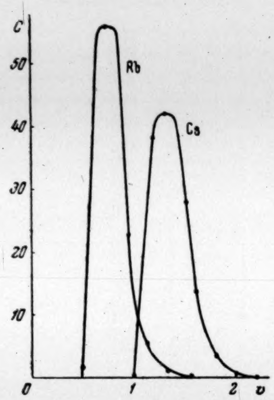
The use of Complexone III for the chromatographic separation of rubidium and cesium has not been described in the literature. The low stability of complexes of Complexone III with lithium and sodium, and the fact that the stability of the complexes usually decreases with increasing radius of the ion being complexed, gives reason for thinking that Rb and Cs do not tend to form complexes. We made a series of tests to study complex formation between Complexone III and Rb and Cs, and the application of this complexone for chromatographic separation of these elements.

First of all we took elution curves for rubidium and cesium. Tests were carried out with columns 100 cm long and 0.5 cm in diameter filled with resin Mark SBS with particle sizes ranging from 0.25 mm to 0.35 mm. The resin was converted into the Na form by passing 10% NaCl through the column, and was then washed completely free of chloride ions with distilled water. 1 mg. equivalent of rubidum or cesium to which had been added Rb^{86} (T = 19.5 days) or Cs^{134} (T = 2.3 years) respectively, as indicators, was then sorbed onto the resin from neutral aqueous solution.

After the original solution had been passed through the column, the latter was washed with distilled water and the sorbed ions eluted with a 1% aqueous solution of Complexone III (pH about 5) at a rate of 2-3 ml/ minute. The eluate was split up into 200 ml fractions. The distribution of rubidium or cesium in the individual fractions was determined from the activity of each fraction.

The reproducibility of the elution curves for each element was checked in replicate experiments on several identical columns. The results of these replicate were in good agreement.

The nature of these elution curves for rubidium and cesium indicate that both elements, under the experimental conditions used, form compounds with Complexone III, the complex with rubidium being more stable than that with cesium, since Rb is eluted before Cs. Judging from the results on separate elution of Rb and Cs, it can be postulated that Complexone III can be used for separating mixtures of these elements.



Elution curves for rubidium and cesium.
C) Concentration of rubidium and cesium in % of 200 ml eluate; V) Volume of eluate in liters.

Elution curves were also taken when 1% Complexone III (pH about 5) solution was used for eluting rubidium and cesium sorbed on resin Mark KU-2. We found that in this case both elements are eluted absolutely simultaneously. This result can be obviously explained by the appreciable swelling of KU-2. On swelling resins, elements whose separation is based on differences in the hydration of the ions are not readily separated [27]. Rubidium and cesium belong to this class of elements.

Experiments on the chromatographic separations of Rb and Cs were carried out by the same technique and on the same columns as those used for taking elution curves of the two elements. The contents of rubidium and cesium in the original solutions were 1 and 0.1 mg. equivalents respectively. This ratio was chosen because in their natural mixtures there is always more rubidum than cesium. The eluent was a 1% solution of Complexone III with a pH of 5. The use of other complexing agents as eluents gave considerably poorer separation.

The results obtained are shown on the diagram. It is evident from this that Complexone III can be effectively used for the chromatographic separation of rubidum and cesium. Under the conditions used 90% of pure Rb and 65% of pure Cs were separated.

Similar results were obtained when the eluent used was a 0.5% solution of Complexone III at the same pH.

In order to get more efficient separation of rubidium and cesium one should use longer columns and reduce the elution rate 2-3 times.

SUMMARY

A short review is given of the most important papers on research into the physical and chemical properties of Complexone III. Results are given of a study into the possibility of using Complexone III for chromatographic separation of rubidium and cesium. The authors managed to separate about 90% rubidium from a mixture of these elements.

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APPLICATION OF THERMOGRAVIMETRY IN ANALYTICAL CHEMISTRY

PART I. A THERMOBALANCE OF SIMPLIFIED DESIGN.

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In thermogravimetry the weight of a material is determined in relation to the temperature or the duration of heating (and cooling as well) at a certain rate. The shape of the thermogravigram (the graphical representation of the change in weight in relation to temperature) for the same material is determined in the first instance by the choice of precipitating reagent (this is true of many metal hydroxides, e.g., those of aluminum, zirconium, etc).

Other factors which affect the shape of the thermogravigram are the atmosphere in the oven, the rate of heating, the amount of material being heated, its compactness, particle size, and shape of the crucible.

The horizontal areas on the thermogravigrams correspond to chemical compounds stable in a definite tempererature range; e.g., on heating calcium oxalate there are formed four stable chemical compounds: the first corresponds to the hydrated oxalate $CaC_2O_4H_2O$, which exists up to 120°; the second to the anhydrous oxalate stable up to 370°; on increasing the temperature further, calcium oxalate decomposes in the range 400 to 550° to form calcium carbonate with evolution of carbon monoxide; calcium carbonate is stable up to 700°. On increasing the temperature further the carbonate decomposes to form calcium oxide; the process finishes at 900°. On the thermogravigram there are horizontal plateaus corresponding to each of these stable compounds (Table 1). This classical example shows that the precipitated calcium oxalate can be weighed in any of these four forms. The range of their temperature stability agrees with the temperatures of their calcining or drying in analytical practice. Thermogravigrams clearly show the behavior of material towards heat, and often make it possible to establish the composition of the compounds formed, including the amount of water of crystallization.

In some instances there can be observed an upward trend on the thermogravimigrams as a result of an increase in weight caused by interaction between test material and the atmosphere.

For example, some oxidizing agents (iodates, bromates, chlorates, nitrates, stannates, etc) before decomposing either reversibly or irreversibly increase their weights, sometimes by as much as 20%, as a result of absorption of oxygen from the air and the formation of peroxides.

By using the thermogravimetric method it is possible to establish the presence of adsorbed water and adsorption of other materials, which is important for controlling washing processes. In some cases it is possible by means of thermogravigrams to calculate the atomic weight of an element, e.g., carbon in the case of calcium oxalate on the basis of the ratio of carbon dioxide evolved during decomposition of the carbonate. Presumably, when this method has been improved sufficiently, it should be possible to determine the isotopic composition of carbon.

Thermogravimetry enables one to study the reaction kinetics of decomposition in the solid phase in which gaseous materials are evolved. Results of the thermogravimetric study of compounds of most elements can be found in the well known monograph of Duval [1].

Thermogravimetry is similar to thermography which was originated by Kurnakov [2]. In thermography it is those changes in the material which are not accompanied by changes in weight but by changes in thermal effects that are observed. Elucidation of processes which occurs in a material, despite successes already achieved [3], is still difficult. Thermogravimetric methods in many instances can be essentially supplemented by results obtained during thermographic studies.

This idea was set forth by Tsvetkov as long ago as 1951 [4], and has proved very fruitful; he also constructed a balance for continuous weighing which was based on the principle of a torsion balance.

Thermogravimetry can be used in analytical chemistry for the following purposes:

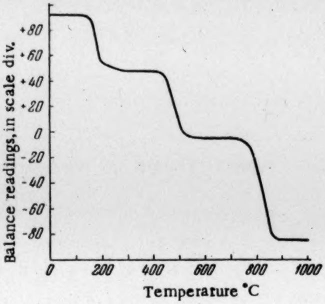

Fig. 1. Thermogravigram of calcium oxalate.

1) In the search for new forms of materials which can be used for their gravimetric determination; determination of the temperature range within which these forms are stable. Establishing the existence of intermediate compounds of low stability.

2) For weighing materials which are unstable at low temperatures, including those which absorb CO_2 and H_2O from the air.

3) For studying the behavior of materials in atmospheres of various gases.

4) For checking the purity of analytical reagents and for determining their content of water of crystalization.

5) For determining components of complex mixtures, e.g., determination of calcite in gypsum, determination of silver and copper in mixtures of their nitrates,etc.

6) For the systematic study of the properties of materials in relation to the methods used for their prepartion; these materials including hydroxides.•

7) For simplifying and speeding up normal gravimetric determinations, particularly when changes in weight and temperature are registered automatically.

The Duval thermobalance is considered to be one of the best designs in existence at the moment [1]. This was constructed on the basis of the Shevenar balance used for studying metal corrosion. In the Shevenar balance the beam is suspended on two tungsten threads. In this way it is possible to eliminate the fundamental drawback of the ordinary analytical balance, in which the prisms of the beam rapidly wear out as a result of prolonged contact with the supports during continuous weighing.

For heating the samples, Duval used an oven opened from below which he arranged above the balance. In this way the thermal effect of the oven on the balance, and the effect of convection on the crucible plus sample which are contained in the oven itself, are both lessened.

In 1952 the Leningrad factory Gosmetr was commissioned by Moscow State University to construct a balance for continuous weighing (Type VR-NV-20) which would be suitable for solving analytical problems.

A brief description of this balance can be found in the paper by Novoselova et al [5].

For simplifying the construction, analytical weights were used in conjunction with a 20 mg optical scale having 200 divisions per 0.1 mg; the small weights were loaded automatically (Meopt type - Czechoslovakia).

• As Duval has shown [1], the behavior of hydroxides at high temperatures depends to a considerable extent on the reagents used for precipitating the hydroxides. Thus in the case of aluminum precipitated by aqueous ammonia, the weight of the hydroxide becomes constant at 1030 deg, whereas on precipitation with gaseous ammonia, pyridine, and ammonium acetate, the weight becomes constant at 475 °.

The general arrangement of the separate parts can be observed from Fig. 2 and 3. The balance 1 was mounted on bearings 2 fixed immovably to the table so as to eliminate side displacement. The table 3 was arranged on brackets in the main wall at a distance of 880 mm from the floor. This height is necessary so that it may be possible to arrange the oven of the thermobalance in the space below the table under the balance. The balance pan was replaced by a suspended system of fine wire 8, ending in a platinum cradle 12 for the crucible which was contained in the oven 13. An arrester with a shorter axis was fitted, and the arm of the arrester drawn into the lower part of the balance, so as to make it possible to lead the wire of the suspended system below through the bottom of the balance into the oven.

In order to neutralize the chaotic vibrations of the beam around the equilibrium position as a result of the effect of convection currents in the heated oven on the crucible, a strong damper was used; this was placed on the balance stage instead of the balance pan. The time constant of the mobile part of the balance under these conditions was 5 seconds.

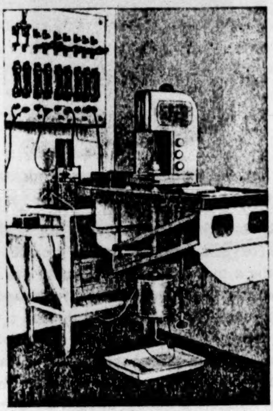

Fig. 2. General appearance of the thermobalance.

The damper consisted of a strong magnet 4 with an annular gap of 2.5 mm (this was taken from an electrodynamic loudspeaker). An opening 5 mm in diameter was drilled along the axis of the magnet through which the wire of the suspended system was passed. An aluminum cylinder 5 forming part of the suspended system was fixed in the magnet gap. The only drawback of this type of damper was the nonlinearity introduced by it into the balance scale. The nonlinearity could presumably be avoided by improving the construction of the damper or using a damper of a different type. All the same we settled for the type of damper described, and used a calibration curve which was also necessary because of the large deviations of the beam at the end of the scale, and because of some drawbacks in the optical system of the scale in the type of balance used.

That part of the wire of the suspended system which is located between the balance and the oven was enclosed in a copper cylinder 6 in order to protect the wire from air currents in the setup.

Baffle plates in the form of cones 7 were placed inside this tube in order to prevent hot air from getting in; these baffle plates led the hot air from the center of the tube towards the edges where there were openings.

Copper wire diameter 0.15 mm was used for the suspended system, while that part of this system found in the oven, and the cradle, were made from platinum wire 0.5 mm in diameter.

The two side screens 10 fixed over the oven completely protected the balance from the action of hot air.

The samples were heated with an oven of 200 watts power operating at a voltage of 127 volts. The nichrome wire spiral was wound on an alundum tube 35 mm diameter. The maximum temperature which the oven is capable of is 1000° at 127 volts. The size of the oven casing was increased in order to improve the thermal insulation. The oven can be shifted vertically along a stand fitted with a rack. The stand was fixed below on the table. The upper stopper of the oven 11, which was made from graphite and had a hole 3 mm in diameter for the wire to pass through, was also fixed securely to the same stand. Thus on letting down the oven to the lower position, the latter is opened at the same time, thereby facilitating loading of the oven. The materials of the oven walls and the upper stopper were chosen so as to exclude the possiblity of foreign material getting into the crucible.

Through the lower stopper of the oven 14, also made of graphite, a thermocouple 15 was passed; the tip of the latter was separated from the bottom of the crucible by a distance of a few millimeters when the oven, which is held in position by an arresting device, is in the operating position. This lower stopper also had

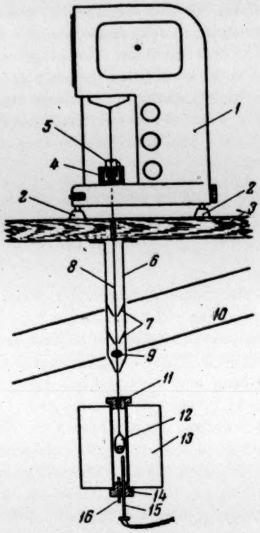

Fig.3. Schematic diagram of the thermobalance.
1) balance, 2) bearings; 3) table; 4) magnetic damper; 5) damper anchor; 6) protective copper tube; 7) conical baffle plates; 8) wire of suspended system; 9) load; 10) screen; 11) oven stopper; 12) planinum cradle for crucible; 13) oven; 14) bottom stopper of oven; 15) thermocouple; 16) inlet tube for gas.

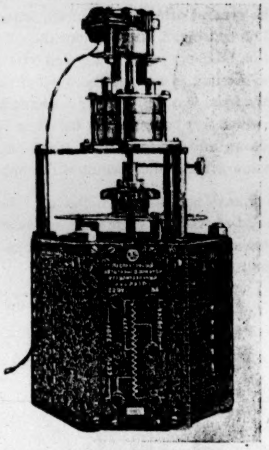

Fig. 4. Laboratory autotransformer with drive.

a hole through which a tube 16 for passing various gases (oxygen, nitrogen, carbon dioxide, etc.) was fitted; the e.m.f. of the thermocouple was registered on a galvanometer graduated in millivolts and degrees Centigrade. The oven was fed through a voltage stabilizer type EPA-27 with a power of 500 watts, and a laboratory autotransformer type LATR-1, which was provided with a synchronous drive from a Warren motor making two revolutions a minute through a 1:1500 reducer (Fig. 4). The axis of the reducer was connected with the handle of the autotransformer through a clutch with a tightening screw which can be freed by shifting the handle of the transformer to the initial position. The rate of change in voltage transmitted to the oven was 21 volts/hour. At an initial voltage of 40 volts on the winding of the oven, and at the indicated rate of change of voltage, heating of the oven was linear and amounted to 3.5°/minute.

Experimental technique when using this thermobalance is exceedingly simple. The oven is lowered to the lowest position, the crucible containing sample is placed in the cradle, the oven then lifted to the upper, working position, and the balance equilibrated so that the scale indicator is at the upper end. Since the smallest rider weighs 10 mg, additional riders ranging from 1 to 5 mg suspended on the hook in the suspended system are used. The weight of sample placed in the oven is chosen such that the total change in weight will not exceed 20 mg. In most cases the sample weight is 30-50 mg.

Determination of the weight of original sample and of the final weight of the material after calcining is carried out on a microbalance.

After equilibrating the balance the current to the oven is switched on as well as the transformer drive, while the readings of the galvanometer of the thermocouple are taken with time. The results obtained are plotted in temperature-weight coordinates.

Materials which had already been studied were used for checking the operation of the balance [1]. The thermogravigrams which we obtained only differed from those which have been described with regard to small shifts in the temperatures of characteristic points on the curve; this is probably related to the smaller amounts of samples (30-50 mg) which we took. Duval used samples weighing about 500 mg.

In addition to calcium oxalate,* whose thermogravigram was considered above we studied neodymium oxalate and two nitrates – those of copper and silver.

Neodymium oxalate was precipitated from a solution 1 N with respect to neodymium and 0.3 N with respect to HCl on heating to 60-70° with a hot solution of oxalic acid (an aqueous solution of oxalic acid saturated with respect to the latter in the cold). The precipitate was filtered after standing for two hours and washed several times with hot water and once with alcohol [6].

The oxalate prepared in this way contains nine molecules of water of crystallization. On the basis of the thermogravigrams obtained (Fig. 5) it can be concluded that the other stable hydrates of neodymium oxalate are the dihydrate and the monohydrate. The first is formed at 145°, and the second at 180°. At 310-335° anhydrous neodymium oxalate is obtained, which starts to decompose rapidly at 350° to the carbonate; this is only stable up to 425°. Decomposition of the carbonate is accompanied by formation of an intermediate compound whose compositiion corresponds to the formula $2Nd_2O_3 \cdot CO_2$ at 625°. Decomposition of the carbonate ceases at 730° with formation of the oxide Nd_2O_3.

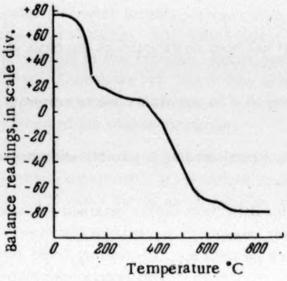

Fig. 5. Thermogravigram for neodymium oxalate.

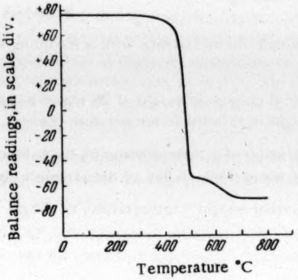

Fig. 6. Thermogravigram for silver nitrate.

Thus, during decomposition of neodymium oxalate two new intermediate compounds have been detected – the oxalate dihydrate and the basic carbonate $2Nd_2O_3 \cdot CO_2$ – which have not been identified on thermogravigrams before; at the same time the existence of a trihydrate could not be established.

In Fig. 6 is shown the decomposition curve for silver nitrate** ; from this it is clear that silver nitrate is stable up to 300°. Decomposition ceases at 700° with formation of elemental silver. A different picture is observed in the case of $Cu(NO_3)_2 \cdot 3H_2O$ (Fig. 7), decomposition of which starts already at 300° with formation of cupric oxide. Slowing down of the decomposition of cupric nitrate at 170-230° corresponds to formation of the stable basic nitrate $Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$. This difference in decomposition temperatures allows one to determine copper and silver as their nitrates when they are present simultaneously. The thermogravigram for mixtures of cupric and silver nitrates is shown in Fig. 8. From the latter it is clear that the basic regularities in the decomposition of these nitrates are preserved in their mixtures.

In conclusion, we should like to point out that even a thermobalance of the simplest construction enables one to get valuable results, which differ to only a small extent from those obtained on such a very complicated and advanced balance as the Shevenar-Duval balance.

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* Commerical calcium oxalate was used for taking thermogravigrams.

** Commerical cupric nitrate and silver nitrate were used for studying their thermogravigrams.

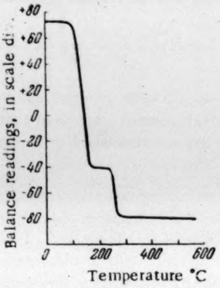

Fig. 7. Thermogravigram for cupric nitrate

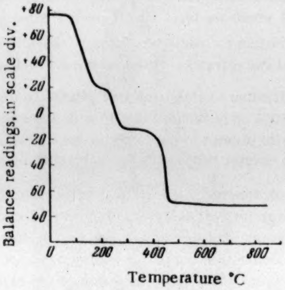

Fig. 8. Thermogravigram for a mixture of cupric and silver nitrates.

SUMMARY

1. A simple thermobalance with a recording weightometer has been constructed on the basis of an analytical balance.

2. A total change in weight of 20 mg on a sample weighing 30 - 50 mg allows one to carry out continuous readings of weight in relation to temperature changes.

3. The value of a scale division on the balance is 0.1 mg. Visual reading is possible with an accuracy of 0.01 mg, this is about 0.02 - 0.03% of the sample weight.

4. Curvesof weight - temperature, or weight - time, differ little from curves obtained on more advance instruments.

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EXTINCTION OF CYANIDE BANDS DURING SPECTROGRAPHIC ANALYSIS OF SOLUTIONS

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The appearance of cyanide bands during the use of carbon electrodes in arc or spark discharges complicates analytical procedure sometimes, and in certain cases makes analysis impossible. Compounds of the alkali metals have been recommended in some papers for eliminating cyanide bands. Thus, Erdey and Gegus [1] used $K_2S_2O_7$ for suppressing cyanide bands in an A.C. arc, and pointed out that compounds rich in oxygen are particularly suitable for this purpose. Hegemman and Leybold [2], during analysis of pyrites in a D.C. arc for its content of thallium, established that it is possible to eliminate interfering cyanide bands by addition of potassium chloride to test samples. Kenan and White [3] used lithium chloride for suppression of cyanide bands in a D.C. arc. Zheenbaev [4] found that addition of sodium and potassium salts to an A.C. arc approximately halves the intensity of cyanide bands. In all the cases adduced above the materials used were in the form of powders placed in the carbon electrode.

Cyanide bands - though somewhat weaker - also appear during spectrographic analysis of solutions by means of carbon electrodes. It seemed of interest to us, therefore, to study the capacity of the alkali metals to suppress cyanide bands during spectrographic analysis of solutions as well.

The work was carried out on a quartz spectrograph (the ISP-22). Spectra of solutions were excited by means of IG-2 and DG-1 generators. The solution was introduced into the discharge gap with a "fulgurator" which has been described earlier [5].

The following conditions were used during photographing of the spectra when an arc generator was employed: an arc discharge, current 2 amperes, gap between carbon electrodes - 1.5 mm, time of firing of arc 5 seconds, exposure time 30 seconds, slit width 0.02 mm; the slit was illuminated by two lenses (one with F 75 cm at a distance of 70 cm from the slit, the other with F 160 cm at a distance of 37 cm from the slit).

When the spark generator IG-2 was used the conditons for photographing were as follows: current 2.6 amperes; self-inductance 0.55 mH; capacity 0.02 μF; electrode distance 1.5 mm; exposure time 1 minute; the slit was illuminated as before; the scheme for switching on the generator was complex.

Negative kine film "Isochrome" with sensitivity 45 units GOST was used, while the positive had a sensitivity of 0.5 units. The development time for the first was 1.5 minutes, while that for the second was 2 minutes. The developer was metol-hydroquinone [6], while the development temperature was 20°.

The film was treated on an MF-2 microphotometer.

First, we studied and compared the capacity of all the alkali metals (as their chlorides) to suppress cyanide bands in the spectra of aqueous solutions. The concentration of test solutions -on the basis of the metal - was 0.25%. The spectrum of distilled water was photographed simultaneously with the spectra of test solutions on the same film. The principal line - 3883.4 A -of the cyanide band was measured photometrically on the films, as well as the most intense line in the spectrum of the solution, and the background created by this band in the region around 3878 A. The absolute blackening of the principal line, and that of the background in the spectrum of water were taken as 100%. The use of absolute blackenings for evaluating the brightness of spectra is not beyond reproach, but it is good enough for establishing the general regularities in the effect of the alkali metals on the intensity of cyanide bands. Results (mean values) of this study are given in Table 1.

As the results given in this table show, suppression of cyanide bands is more effective in an arc, and suppression increases with decreasing ionization potential of the element added to the solution.

In subsequent work we used the more readily available salts of potassium, the concentration of potassium in the solutions being 0.5%.

Tables 2 and 3 (only arc spectra) contain results relating to the capacity of various potassium compounds to suppress cyanide bands in the spectra of solutions (1 and 2 are used in the same sense as in Table 1).

On the basis of the results contained in Tables 1 and 2 it is impossible to detect any general rule regarding the capacity of potassium salts to suppress cyanide bands. Increasing the concentration of potassium salts in solution leads to considerable suppression of cyanide bands in the spectra of solutions (Fig. 1). The absolute blackening of the principal line in the cyanide band, and that of the background in the water spectrum, photographed simultaneously on the same film, were taken as 100%. The use of potassium salts for suppressing cyanide bands and background leads, however, to some weakening of all the spectrum. The extent to which the spectrum as a whole is weakened depends on the nature of the element.

TABLE 1

Material	Excitation source			
	Arc		Spark	
	1*	2**	1	2
Water	100	100	100	100
LiCl	89	78	99	94
NaCl	83	57	88	69
KCl	80	50	87	64
RbCl	76	50	68	52
CsCl	62	48	65	50

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* The absolute blackening of the principal line of the cyanide band is taken as 100%

** Ditto for the background.

TABLE 2

Material	Excitation source			
	Arc		Spark	
	1	2	1	2
Water	100	100	100	100
KCl	74	50	81	64
KBr	60	60	80	69
KI	70	41	—	—
KOH	27	33	52	31
K_2CO_3	27	35	55	36
KNO_3	63	37	78	61
K_2SO_4	65	50	85	75

TABLE 3

Excitation source DG-1					
Material	1	2	Material	1	2
Water	100	100	KSCN	58	28
$KClO_3$	76	56	C_2O_4HK	74	48
$KClO_4$	96	93	$C_2H_4O_6K_2$	53	25
K_2CrO_4	64	34	$C_6H_5O_7K_3$	60	33
$K_2Cr_2O_7$	68	37	$K_3[Fe(CN)_6]$	69	—
$KMnO_4$	53	30	$K_2S_2O_7$	58	29

TABLE 4

Material	Excitation source			
	Arc		Spark	
	1*	2*	1	2
Water-upper carbon electrode	100	100	100	100
Water-upper copper electrode	94	93	96	95
KOH— "	17	10	61	40
K_2CO_3— "	13	8	54	37
KCl— "	25	18	55	36
KBr — "	15	13	59	39
K_2SO_4— "	15	15	50	35
KNO_3— "	14	12	56	36

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* Обозначения 1 и 2 — те же, что в табл. 1.

Thus, in the case of the lines CrI 3963.7 and CrI 3976.6 in an A.C. arc, on addition of K_2SO_4 (0.5% calculated as K) to the solution, the first line weakens by 14%, while the second weakens to the extent of 16% in terms of absolute blackening. The blackening of copper lines CuI 5105.5 and CuI 5153.2 falls by approximately 18% on addition of KBr (0.5% on a K basis) to the solution. The lines in the magnesium spectrum MgII 2798.0, MgII 2790.8, MgI 2781.4 and MgI 2776.7 A are less sensitive to additions of various potassium salts; their absolute blackening decreases by 2-3% in an A.C. arc.

Another technique for suppressing cyanide bands is to use a second electrode made of metal, e.g. copper.

The use of only one copper electrode during spectrographic analysis of a solution is not very effective, and depression of the cyanide bands and the background amounts to only 4 - 6%. All the same, the simultaneous use of an upper electrode made of copper, and addition of a potassium salt to the solution (0.5% concentration in terms of potassium) leads to considerable suppresion of cyanide bands and background (Table 4).

The simultaneous use of an upper copper electrode and addition of alkali metal salts affects the absolute blackening of the lines of various elements present in solution to different extents. E.g. the blackening of the calcium lines Ca II 3936.6 and Ca II 3968.4 decreased from 3 - 4% on adding KNO_3 (0.25% on a potassium basis), while the blackening of the calcium line Ca I 4226.7 increased by about 5% in an a.c. arc. Blackening of the nickel lines Ni 3374.2, Ni I 3414.7 and Ni I 3524.5 in an a.c. arc decreased on an average by 12% on adding KCl to the solution (0.25% on a potassium basis).

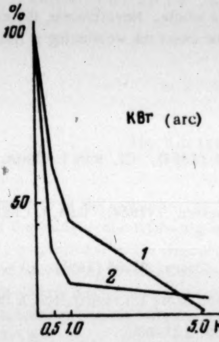

Fig. 1.

Finally, calibration curves were constructed on the basis of the lines lying in the region of the cyanide bands. The spectra were excited by an arc generator; both electrodes were carbon.

Those shown on Fig.2 are for the lines Fe I 3841.0 / 3840.4 Mg I 3838.2 and Cr I 3841.2; while those on Fig. 3 are for the lines MgI 3838.2 Cr I 3841.2. 1 - on the diagrams designate solutions to which no potassium had been added and 2 those to which K_2SO_4 had been added (0.5% on a potassium basis).

Addition of potassium salts during spectrographic analysis of solutions increases the linear part of the curves, and increases the slopes of the calibration curves for lines lying within the cyanide bands.

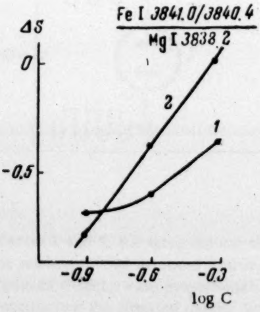

Fig. 2

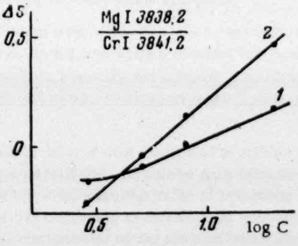

Fig. 3

SUMMARY

1. Addition of alkali metal salts during spectrographic analysis of solutions suppresses cyanide bands. The alkali metals, in virtue of their low ionization potentials, lower discharge temperatures, leading thereby to weakening of cyanide bands.

2. Suppression of cyanide bands during spectrographic analysis of solutions improves the slope of the calibration curve constructed on the basis of the analytical pairs of lines falling within the cyanide bands, and increases the range over which the curve is linear.

3. Addition of alkali metal salts usually weakens the spectrum as a whole. Nevertheless, the extent of weakening of the spectrum for various elements is not the same; in some cases the weakening is insignificant, and does not essentially affect the sensitivity of a determination.

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IMPROVEMENTS IN THE TECHNIQUE OF CONDUCTOMETRIC TITRATION

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When two of the resistances in opposite arms of a Wheatstone bridge are constant, then during equilibration of the bridge, the following relation holds for the other pair of resistances: the resistance of one arm is directly proportional to the conductivity of the opposite arm. This fact has been used by one of us for speeding up and simplifying conductometric titrations [1]. In the apparatus constructed for this purpose, use was made of a sliding contact specially made and having a very low and constant intermediate resistance [2]. The use of this contact ensures reliable accuracy in measurements of electrical conductivity; the construction of this contact, however, is rather complicated, and during operation demands continuous attention which is a drawback. Below we have given a description of tests on another scheme which we have developed where this drawback has been overcome.

The scheme shown in Fig. 1 is the usual Wheatstone bridge. A sound frequency generator is connected to terminals 1 and 8, the null-instrument is connected to terminals 4 and 6. A characteristic of this setup is that the rheocord 2 has a low resistance, while resistance 3 is chosen to be as high as possible. Because of this value of the resistance of the arm of the bridge which includes resistance 3 and that part of rheocord 2 from the movable contact to the point where it is connected with resistance 3 it can be assumed that during titration the resistance can be regarded as constant. The intermediate resistance of the sliding contact has hardly any effect during operation.

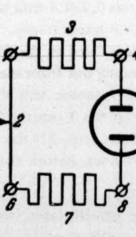

Fig. 1.

For satisfactory operation of this setup, a sound frequency generator which operates steadily and a sensitive null-instrument are necessary. The optical indicator 6E5 with preliminary two- or three cascade amplification on pentodes is particularly suitable as the null-instrument. We used the amplifier which has been described previously by one of us [1], but it is possible to use other schemes [3], or ready made apparatus.

Two setups were made in order to test out the operation of this scheme. In the first variant ordinary laboratory apparatus was used: rheocord 2 was the usual linear type, 1000 mm long with a resistance of 4,2 ohms. Resistances 3 and 7 were decade boxes type KMS-6.

Titrations of acid with alkali and of sodium tetraborate with acid were carried out. As can be seen from the results given in Tables 1 and 2, the setup ensures satisfactory accuracy even when the value of resistance 3 is only 10 ohms. The readings of the rheocord (initially the rheocord was connected to terminal 6) corresponding to added volume of titrant, were proportional to the electrical conductivity of the solution being titrated, and were used for constructing the titration curve. Volume of titrant was plotted along the abscissa while rheocord readings were plotted along the ordinate. When using this type of scheme there is no need to make any calculations before constructing a titration curve. Consequently, a titration curve can be constructed during actual titration.

TABLE 1

Conductometric Titration of Acid with Alkali. Concentration of H_2SO_4 and NaOH Solutions About 0.25 N. In all Tests the Volume of Solution Being Titrated was 50 ml; for Titration of H_2SO_4 the Volume Taken was 0.500 ml.

Resistance 3 in ohms	Resistance 7, in ohms	Amount in ml of NaOH used for titration.
First variant		
1000	0.7	0.448
1000	0.7	0.452
1000	0.7	0.452
1000	0.7	0.448
100	11.7	0.450
100	11.7	0.448
100	11.7	0.450
100	11.7	0.450
10	112	0.448
10	44.3	0.452
Second variant		
		0,449
		0,450
		0,450

When the electrical conductivity of the solution being titrated attains a constant value fairly quickly, then, after some practice, only takes 8-10 minutes to carry out a titration, including plotting the curve.

In the second variant of this setup an apparatus was used for constructing the titration curve at the same time as titration was actually being carried out, whereby it was possible to eliminate the need of making notes of the readings of the rheocord.

In this setup resistance 3 was an alternating radio-resistance with a value of 5000 ohms, while resistance 7 was 0.4 ohm and consisted of a piece of constantan wire. Rheocord 2 was a piece of constantan wire 24 cm long and 0.4 mm in diameter, and having a resistance of 0.9 ohm. The rheocord was mounted on the longer side of a school drawing board 25 x 33 cm, and 2.5 cm thick. The sliding contact was arranged on the arm of a square lying adjacent to this same drawing board; the contact was a strip of type metal brass 0.3-0.4 mm thick and 6-8 mm wide bent into the shape of the letter Г, the arms of which were 20 and 10 mm respectively. The edge of the short side was rounded off by bending a narrow strip of the metal. Terminal 1 was fixed to the middle of the T-square arm and the long side of the strip soldered to the bolt of the terminal sticking out from the other side, so that the short side with its rounded edge pressed lightly on the rheocord when the T-square arm was adjusted along the edge of the drawing board. It was found best to replace the straight-edge of the T-square by a measuring rule with bevelled edges, the latter being screwed or glued to the upper side of the arm. All the remaining details of the setup can be arranged on the same drawing board near one of its short sides. Before commencing titration a sheet of paper was placed on the board and stuck down along one edge.

The sliding contact was arranged in the initial position chosen and the bridge equilibriated first by changing the radio resistance 3, and then, finally, by small forward movements of the movable contact, during which the arm of the T-square was pressed slightly to the edge of the board (in order to avoid shifting all the apparatus during operation, one can fix fine vacuum rubber tubing beneath the drawing board along its edges). After the bridge had been equilibriated, while holding the T-square in the position found, a point was marked opposite the null point of the scale with a sharply pointed drawing pencil. Next the first aliquot of titrant was added, the solution was mixed, and the bridge again equilibriated by forward movement of the T-square with movable contact, the points being plotted opposite the divisions of the straight-edge, corresponding, under the scale chosen, to the volume of titrant added; this procedure was then repeated for all points until a complete titration curve had been obtained.

After plotting the points they were joined up and the volume of titrant corresponding to the point of intersection of these lines determined from the scale of the straight-edge which was moved up to this point for this purpose. Details of the procedure used for titration with a device of the type described have been given in an article already cited [1].

The second variant of the apparatus was also checked on the same materials as those used for the first variant. The results which are given in Tables 1 and 2 show that satisfactory accuracy can be achieved. After practice a titration can be carried out on the second variant in 5-6 minutes. This setup can be constructed easily and costs very little.

Using the second variant of the scheme we also carried out titrations in the presence of another electrolyte. As the results in Table 2 show, when there is an appreciable excess of another electrolyte present, the accuracy of determination drops. Apart from other reasons, this is the result of inaccuracies in establishing the point of intersection of the lines on the diagram, since the angle between the lines obtained under these conditions is very obtuse.

A cylindrical lens which could be easily prepared proved very useful in cases of this type. A lens could be prepared by preparing an ampoule 6-7 cm long from glass tubing 9-10 mm in diameter with thin and even walls; this ampoule was filled with benzene, carbon tetrachloride, or even, in extreme cases, water, and then sealing the tube so that a small bubble of air remains inside. Two rubber rings 1 mm thick are fitted round the ends of the ampoule. In order to establish the point of intersection, the lens is placed on the diagram so that its longitudinal axis lies over the point of intersection and is perpendicular to the bisectrix of the obtuse angle. For this position of the lens, the point of intersection is defined far better; with the aid of a fine ruler a third line is then drawn at approximately right angles to the axis of the cylindrical lens. All this takes very little time. After this the common point of intersection of the pencil of three lines can be readily found. The accuracy of the reading will be higher, the finer the lines drawn on the diagram. This cylindrical lens may also be useful in polarography and amperometry.

TABLE 2

Conductometric Determination of $Na_2B_4O_7 \cdot 10H_2O$ with Standard H_2SO_4. Volume of Solution Titrated 50 ml.

Normality of solution being titrated.	Salt taken in mg.	Amount of titrant used in ml.	Salt found in mg.	Error in mg.	Notes
		First variant			
0.0014	13.2	0.287	13.4	+0.2	
0.0022	21.5	0.465	21.7	+0.2	
0.0030	28.3	0.600	28.0	−0.3	
0.0037	35.4	0.758	35.4	0.0	
		Second variant			
0.0010	9.3	0.199	9.7	+0.4	
0.0017	16.2	0.344	16.1	−0.1	
0.0032	31.0	0.662	30.9	−0.1	
0.0020	19.0	0.407	19.0	0.0	The solution contains NaCl at a concentration of 0.02 N
0.0020	19.0	0.401	18.7	−0.3	ditto 0.04 N
0.0020	19.0	0.418	19.5	+0.5	ditto 0.04 N

SUMMARY

A simple scheme is described for speeding up and simplifying conductometric titration. Using the scheme described it is possible to carry out a conductometric titration – including plotting a titration curve – in 5-6 minutes, there being no need to carry out any calculations of electrical conductivity. Results of tests carried out with this scheme show that the accuracy of determination is satisfactory.

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AN APPARATUS FOR THE MICRO ANALYSIS OF INERT GASES

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During normal gas analysis the inert gases remain with nitrogen. In those cases where it is necessary to determine their amount, so called "crude nitrogen", i.e., nitrogen plus inert gases, is analyzed in a special apparatus.

At present the most widely used method for determining inert gases is that of Paneth [1], which has been developed in Russia by Khlopin and Gerling [2], Sokolov [3], and Cherepennikov [4]; it consists essentially in absorption of nitrogen and other possible gaseous impurities by fused metallic potassium. The inert gases which are left are separated by absorption on activated charcoal at the temperature of liquid air into the heavy inert gases – argon, krypton, xenon – and light inert gases helium and neon. Their further separation is effected by distillation at low temperatures, while for determination of helium and neon, resort is often made to the thermal conductivity method (Paneth [5], Sokolov [2]). Sometimes spectroscopic methods are used.

Apart from difficulties connected with the similarity in their properties, there is the additional difficulty of considerable differences in their relative proportions in natural products. Thus, in the atmosphere the ratio of argon to xenon is approximately 100,000 to one. As a result it is normal practice to confine determination to the sum of heavy and light inert gases respectively.

Paneth's apparatus [5,6] has a large number of taps in the vacuum side of it; this rather complicates making such an apparatus. Accordingly in the apparatus of Gerling [7] and Sokolov [3] use is made of mercury seals. The significance of this fact becomes apparent when one remembers that for a minimum amount of inert gas for analysis of $1 \cdot 10^{-5}$ ml, in an apparatus with a volume of 1–2 liter, it is necessary to have a vacuum of the order of 10^{-7} mm, which, in itself gives rise to difficulties under the conditions obtaining in a static system with no continuously operating pump.

The apparatus which has been developed at the Institute of Geochemistry and Analytical Chemistry has proved itself in practice; it is characterized by relative simplicity of construction and the range which it covers. The apparatus can be operated either on basis of the circulation method or by the "infusion" method.

The apparatus consists of two main parts.

The first part serves for measuring the gas and for its general analysis by combustion over CuO and Cu, and fractional freezing; it consists of a gas buret, an oven filled with CuO and Cu which is independently heated, and two traps for freezing out.

The second part (the one shown in the diagram) is used for analyzing inert gases, and is isolated from the first part of the apparatus by a vacuum tap Vt; through this tap the gas consisting of the nitrogen residue, or simply natural gas of known composition, can be let into the apparatus for analysis of its content of inert gases; the apparatus is pumped out through it.

For measuring gases which differ considerably in volume we used two compression manometers with arcs A and B, which are capable of stopping the flow of gas from one part of the apparatus to the other. The

The volumes of the separate parts of the apparatus were carefully calibrated; this obviates the need for pushing all the gas through the measuring part of the apparatus, to which one has to resort when dealing with small amounts of gas.

Two reservoirs with mercury D and C, apart from controlling the manometers, also allow one to overlap in succession seven mercury seals arranged at different heights - 1, 2, 3, 4, 5, 6, and 7 and the interchangeable taps. This arrangement is very easy to set up, and speeds up the work but it does require some attention in operation.

For convenience in controlling the mercury, three-way crescent shaped taps I and II which serve for controlling all the apparatus, are connected to the reservoirs by rubber tubing, and are placed in a position most convenient to the analyst. They can be operated simultaneously by both hands. Reservoir C (tap I) closes successively seals 1, 2, 5, and 4, while reservoir D (tap II) controls seals 7, 6, 3.

The compression manometers A and B which are used for extending the scope of measurements consist of a series of vessels of successively decreasing volumes (A - 400 and 40 ml for a capillary diameter of about 3 mm, and B - 450, 10, 2, and 0.5 ml for a capillary of about 0.6-0.7 mm); these in conjuction with the V shaped manometer M allow one to operate with volumes of gas ranging from 100 ml down to $1 \cdot 10^{-5}$ ml.[*]

A constructional detail of manometer B is its combination with a small manometric tube T to increase the limits of measurement to 10^{-7}- 10^{-8}ml.

The total height of the arc from the lower level of the mercury should be a little greater than 760 mm, and measurements are made by slight adjustments of the mercury through taps I and II, which is conveniently accomplished by means of a rubber reservoir fitted onto the side tubes of the taps. The tap pins should not be sickle-shaped, but straight at the ends for good support for the hand.

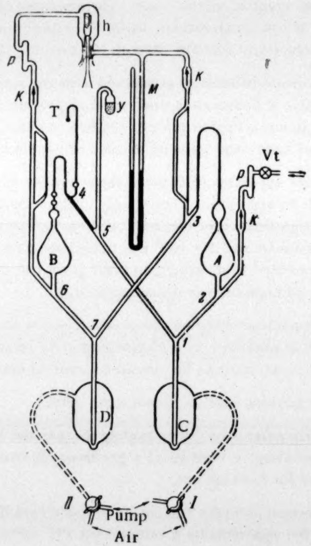
The combination of compression manometer and the heat effect which we used is not new and only differs in constructional details; in principle the method consists of compressing the gas several times and measuring its thermal conductivity. We did not place the thermal manometer which is in the form of a small loop of tungsten wire directly in the capillary of the Mcleod gauge as Pfund did, so that we were able to avoid deformation of the end of the capillary and the inaccuracies connected with this, and were able to ensure satisfactory operation of the thermal manometer at an arbitrarily chosen temperature; this is of great importance.

A manometer with an arc has considerable advantages since it can be used for pumping gas with the same sensitivity as is usual for a Mcleod gauge.

The thermal resistance manometer was made from a tube used for telephone commutators and had a resistance of the order of 10 ohms when cold.

Some difficulty was encountered in fusing the leads of platinite into the molybdeum glass which we used; nevertheless we did succeed in getting a completely hermetically sealed joint.

The volume of such a manometer varies from 0.1 to 0.25 ml and is connected to the apparatus via



Schematic diagram of the apparatus for micro-analysis of inert gases.

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[*] When the manometer is being mounted, A and B are fixed on such a level that the arc of manometer A is 2-3 cm higher than that of manometer B in order to avoid excessive flow of mercury during measurement.

a capillary of the same diameter as that of the compression manometer in order to ensure measurements of absolute pressures on the mercury manometer. A similar manometer is made independantly in which is included a drop of mercury, after which it is evacuated and sealed off. This manometer acts as a compensator for the external conditions.

Manometer and compensator serve as two opposite arms of a Wheatstone bridge in the diagonal of which a sensitive galvanometer is included.

Measurements are carried out at a constant value of the current supplied, thereby ensuring heating of the manometer filament to a temperature of about 100° when the current has a value of 40 milliamperes at 2.4 volts. The constant arm of the bridge has a resistance of 100 ohms. Under these conditions all measurements of the resistance of the equilibriating arm varied from 95 to 183 ohms, i.e., by approximately 90 ohms, at a pressure changes from 1 mm to vacuum. Using a galvanometer with a sensitivity of $5 \cdot 10^{-7}$ amperes and an internal resistance of 195 ohms it is possible to measure the resistance of the manometer with an accuracy of up to 0.01 ohm,

One drawback of the manometer is its nonlinear response so that it has to be calibrated before hand. On using the combination of this manometer with the compression manometer, the highest sensitivity obtained corresponds to pressures of $1 \cdot 10^{-5} - 5 \cdot 10^{-3}$ mm, while the limiting sensitivity amounts to 10^{-8} mm Hg.

By placing the manometer in a vessel containing liquid air as Ellet and Zabel did [8], it is possible to increase the sensitivity of the thermal manometer two to seven times, according to the internal resistance of the galvanometer. In such cases it is advisable to insert a grain of activated charcoal for supplementary adsorption of all gases apart from helium and neon.

The combination of thermal and compression manometers enables one to determine the composition of binary mixtures of gases and to increase the limiting sensitivity of measurements appreciably; there are three possible cases* :

1. Pressures in the apparatus ranging from 10^{-8} to 10^{-5} mm are measured by means of the thermal manometer after compression. In actual practice the thermal conductivity of gases of known composition is measured.

2. Pressures ranging from 10^{-5}-$2 \cdot 10^{-4}$ mm. Pressure is measured by means of the mercury manometer and the thermal conductivity by means of the thermal manometer; after which, using calibration curves, the composition of a binary mixture (helium and neon) can be determined with an accuracy of 5 to 25%.

3. The pressure of the gas exceeds $2 \cdot 10^{-2}$ mm. The composition of the mixture is determined from the readings of the thermal manometer with an accuracy of 2-5% (after compression), while the total amount of gas is determined by means of the compression manometer.

The transition from the second to the third case is determined by the fact that at pressures greater than 20-40 mm, the thermal conductivity of a mixture of helium and neon does not depend on the pressure (Gerling [9]). In the latter case- determination of a binary mixture of gases on the basis of thermal conductivity - using the type of manometer described , less than 0.1 ml of gas is necessary.

At pressures in the apparatus which are greater than 10^{-3} mm, the thermal manometer can be used directly without preliminary compression.**.

Another constructional innovation is the tube-oven with internal heater for combustion with calcium; we have described it in a special article [10] and accordingly we shall only give a brief description of it here.

* The range of pressures measured can be changed by carrying out measurements at different values of the current used for heating the manometer tube filament.

** The spare lead on the manometric tube was used also for transferring measured amounts of purified gas to the next apparatus (mass spectrometer). In such cases, an ampoule for the gas is fused through the frozen mercury seal [11] instead of the manometric tube T; this ampoule can be fused on or off without destroying the vacuum in the apparatus. Argon for isotopic analysis is usually kept in an ampoule containing activated charcoal which is fused in beyond tap Vt.

This tube-oven is a small quartz test tube (about 4 cm long) containing calcium, wound with a heating spiral of nichrome and fitted in a glass vessel of the type normally used for calcining.

In a tube-oven of this type there is an appreciable temperature drop, while the walls of the vessel do not become hotter than 200° although the spiral is red hot. The reaction proceeds mainly with vaporized calcium, while the products formed stay on the vessel walls and are not subjected to thermal dissociation.

In practice complete removal of nitrogen and other gases in the apparatus is attained in 20-30 minutes, and even hydrogen is absorbed quite well; the latter being rather difficult to accomplish in a calcium oven of ordinary construction.

It is easy to excite a luminescent discharge in such a tube and this speeds up gas absorption even more. We used a 3-4 ampere current at a voltage of about 45 volts for heating the tube; the diameter of the nichrome wire was 0.35 mm.

We made tubes of two kinds: one with a hermetically sealed vessel, and one with a ground glass joint for renewing the calcium; both work quite well.

The purity of the gases being analyzed is controlled by means of their spectra, which are obtained during high frequency ionization in the manometer capillary. For this purpose we used a styloscope with a specially constructed objective.

The heavy inert gases are absorbed in a vessel (volume about 2 ml) with activated charcoal Y, which is closed by mercury seal 5. For ease of operation and to avoid throw-over of mercury, three mercury valves K are introduced into the apparatus.

Two traps with baked P_2O_5 are used for drying the apparatus; this is particularly important if moist gas should get into the apparatus straight from the cylinder containing the test sample.* The P_2O_5 was sintered as follows: 2 tubes of molydenum glass, one about 8 mm in diameter and the other about 15 mm diameter, are taken and placed one inside the other. The space between the tubes is filled with P_2O_5 and the ends sealed off. The tube is heated on a gas burner until the glass softens and it blows out as a result of its internal pressure. After uniform heating all along its length, the sintered phosphorus pentoxide in the form of broken pieces or lumps is loaded into the trap which is either fused off or closed with a ground glass joint.

The apparatus which is made of molybdenum glass should be prepared for operation by preliminary treatment to get rid of impurities from the surface of the glass; calcium and charcoal should also be freed from absorbed water vapor and gases, after which the individual parts are calibrated.

Analytical Procedure

Mercury is lifted into the pumped out apparatus by means of tap II so that the mercury covers seal 3, while seal 1 is covered by tap I. After this an aliquot of gas sample is let into volume A through the inlet tap Vt. A small amount of gass is measured by the compression manometer A; larger amounts of gas are measured by the same manometer after distribution of the gas into the upper part of the apparatus through seal 3, while even bigger amounts are measured by a V-shaped manometer with A either empty or filled with mercury. The residue of the gas up to seal 2 can be pumped into the apparatus or discarded, according to the amount of gas. After this has been done, seal 2 is closed and is not opened until completion of the analysis.

The heater of calcium lamp h is switched on and absorption of the gas is followed on the V-shaped manometer. Absorption is speeded up by mixing the gas; this latter is achieved by sucking in and compressing the gas in vessel A by operating tap I (seal 3 is kept open during this operation).

That absorption is complete is checked by observing whether the readings of manometer A are constant; for this purpose the gas in the vessel is stoppered by means of seal 3, the mercury being brought up by means of tap II to the mark on the capillary. The gas in vessel A is then lifted up, and the mercury is adjusted to the mark on the capillary again; from the differences in readings of the capillary the readings of the V-shaped manometer are subtracted. It is possible to check on the spectral purity of the inert gases.

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*Analysis is fastest when nitrogen residues are being analyzed, but determination of inert gases is also possible on individual samples; it is desirable that carbon dioxide be removed from them without resorting to combustion, since the latter will lead to the gas being diluted by air. We succeeded in analyzing gas containing more than 90% of methane and other inflammable gases. Nitrogen should be determined beforehand.

Results of Determinations of Inert Gases

Sample No.	Test material	Gas taken in ml.	Main components of the gas, in %	Found in ml, 10^{-3}		In % by volume	
				Ar (Kr+Xe)	He+Ne	Ar (Kr+Xe)	He+Ne
279	Gas from the bottom of Lake Baikal	16.06	CH_4—86; N_2—11	41.23	0.206	0.257	0.00128
374	Marsh gas from Siberia	18.8	CH_4—74; N_2—22	78.01	0.060	0.416	0.00032
81	Gas from a well	35.78	CH_4—88; H_2—11	57.50	0.137	0.161	0.00038
407	Gas from water well, Yakutya	13.22	CH_4—55; CO_2—27; N_2—16	117.9	0.242	0.891	0.00183
501	Geyser source, Kamchatka	19.34	CO_2—54; N_2—44;	188.2	0.418	0.972	0.00216
264	Well, 1000 meters	9.81	N_2—95	54.96	188.8	0.51	1.93
364	Hydrogen sulfide water, Siberia	19.71	N_2—72; CH_4—20; CO_2—8	318.5	0.22	1.615	0.0518
364	Duplicate on another apparatus	13.7	N_2—72; CH_4—20; CO_2—8	235.2	6.77	1.706	0.0494
463	Water source, Siberia	21.7	N_2—93; O_2—5	409.3	0.605	1.886	0.00266
463	Duplicate	22.8	N_2—93; O_2—5	428.6	0.628	1.880	0.00276
754	Gas isolated from granite	33.74	H_2—51; CO—44	24.2	0.160	843*	5.52*
754	Duplicate	33.49	H_2—51; CO—44	24.4	0.163	848*	5.67*
CA	Gas from a meteorite (10 g)	—	Not measured	—	0.035	—	0.35*
CA	Duplicate (25.14 g).	—	" "	—	0.089	—	0.354*

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* Given in ml x 10^{-3} ml per 100 g sample

The sum of the inert gases is measured by means of manometer A after the oven-tube C has cooled down.

After the sum of the inert gases has been measured, seal 4 is closed by means of tap I and the sum of the inert gases is again measured by means of manometer B as a control, the gas being let into the latter through seal 6 by means of tap II. The gas can be collected in the thermal manometer T by means of a series of transfers; its pressure can be measured by any combination of the thermal manometer and manometer B. Seal 5 is opened by means of tap I, the mercury being let down to a mark below it; the heavy inert gases are absorbed by activated charcoal Y immersed in liquid air. The unabsorbed helium and neon can be measured by manometers B and T, applying a small correction (about 5%) for the volume and partial adsorption in charcoal Y, after which they are pumped through with seal 1 open (tap I) and seal 3 closed (tap II). After pumping these gases off the mercury is brought up to the mark round seal 5, and the pressure of the argon desorbed from the charcoal measured by means of manometer B (and T); argon can also be determined from the difference in the sum of the inert gases and helium. Pure argon can be transferred into the vessel with cooled activated charcoal placed directly beyond tap Vt for isotopic analysis, or is pumped off.

If during the time that the pressure of the argon is being measured, spectroscopic observation shows that it is contaminated, it can be passed through another cycle of purification over the calcium, taking the gas into vessel A through seal 1 and letting it go through seal 2 into volume h.

The simplicity and convenience in operation of this apparatus lead us to recommend it for use in laboratories which carry out gas analysis.

Upwards of 500 analyses have been carried out on this apparatus on various types of gas mixtures. In the table are given some examples of determinations of the content of inert gases in mixtures of various composition, which had not been subjected to preliminary absorption of active gases.

SUMMARY

A simple and reliable apparatus is described for the micro-analysis of inert gases. By means of this apparatus it is possible to determine the sum of the heavy inert gases (Ar + Kr + Xe) and to determine He and Ne separately.

2. The absence of taps in the high vacuum part of the apparatus means that the apparatus is easy to make and is reliable in operation.

3. The use of mercury seals arranged at different heights and operated by two taps enables work to be carried out conveniently by various methods.

4. The scheme used for purifying and measuring the gas allows one to work over a large range of gas volumes: 200 to 10^{-6} ml.

5. The apparatus can be recommended for wide application in laboratories carrying out gas analysis particularly for the analysis of natural gases.

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DETERMINATION OF OXYGEN, HYDROGEN, AND NITROGEN IN MOLYBDENUM, TUNGSTEN, AND NIOBIUM

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Determination of gases in molybdenum, tungsten, and niobium have been carried out on an apparatus devised at the V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry [1].

Determination of hydrogen in the metals indicated does not present any additional difficulties, since neither molybdenum nor tungsten react chemically with hydrogen. Hydrogen only dissolves in molybdenum and tungsten in small amounts; on heating, hydrogen is readily released from these metals. Hydrogen can dissolve in appreciable amounts in niobium. The solubility of hydrogen in niobium is proportional to $\sqrt{p}$ until attainment of equilibrium values which corrrespond to formation of hydrides. Solubility decreases with increasing temperature. This enables one to remove dissolved hydrogen on heating in a vacuum. There is no definite information available regarding the dissociation of niobium hydride. Nevertheless, it can be presumed that niobium hydrides should, like the hydrides of other metals, dissociate at a temperature near to the temperature at which they are formed, but under such conditions that the vapor pressure of hydrogen above the hydride will be lower than the dissociation vapor pressure at the given temperature.

The most common compounds of molybdenum, tungsten, and niobium with oxygen are – WO_3, MoO_3 and Nb_2O_5, respectively. There are indications in the literature that on heating MoO_3 and WO_3 to a temperature of 1750° no dissociation occurs; they can be evaporated at about 1000° without decomposition. All the same these oxides can be reduced to the corresponding metal by means of hydrogen or carbon monoxide.

Pure niobium pentoxide melts at the fairly low temperature of 1520°. On heating this pentoxide to higher temperatures it can be evaporated without decomposition.

There are also published indications that Nb_2O_5 can be reduced with carbon.

An iron bath was used by Sloman [2,3] for determination of gases in molybdenum and tungsten.

As a result of preliminary experiments with niobium, the authors of the present article established that it is possible to use an iron bath for determination of gases in niobium also.

Molybdenum, tungsten, and niobium dissolve in molten iron to form alloys with melting points which are lower than the melting points of the metals themselves. Iron readily dissolves carbon; consequently, the alloys formed between tungsten, molybdenum, or niobium with iron are in good contact with carbon. This fact creates favorable conditions for complete reduction of the trioxides of molybdenum and tungsten and of niobium pentoxide.

On the basis of thermodynamic data it is possible to calculate the temperature at which reduction of metal oxide by carbon in the presence of molten iron occurs. Such calculations for molybdenum, e.g., give a temperature of about 1550°.

In molybdenum and tungsten, apart from chemically combined oxygen, there may be present dissolved carbon monoxide which, however, is readily removed at a temperature of 1000°.

The presence of nitrides Mo_2N, W_2N and NbN, is highly probable (according to X-ray studies).

Dissolved nitrogen may also be present in the metals indicated. The conditions chosen also ensure complete removal of nitrogen.

During analysis involving an iron bath an additional step is added – degasification of the iron. When the crucible has been degassed, 13-15 g of iron is added to the crucible without breaking the vacuum and the iron degassed in turn for an hour at 1800°. A blank is then run, and this is followed by an actual analysis of test sample.

The weight of molybdenum samples is 2–3 g, while that for tungsten and niobium is 1–1.5 g. Before being loaded into the apparatus samples are washed with carbon tetrachloride. Gases are removed from samples

at 1650° in the course of 15 minutes. In the method proposed by Sloman for determination of gases in tungsten and molybdenum, gases are extracted from samples at 1550°. The reproducibility of the results obtained is, however, better at 1650°.

Before analysis of each subsequent sample, 3-4 g of iron is added without breaking the vacuum, and is degassed at 1800° for a half hour. Degassing of iron over a longer time than that indicated is not recommended, because of formation of a solid film of a solution of carbon in iron on the surface of the molten iron, and this film can prevent the sample from immersing in the iron.

Up to 6 samples can be analyzed in one crucible. This is determined by the fact that at concentrations of molydenum in the iron bath of more than 30%, and of more than 20% of niobium and tungsten, there is a danger of getting low results for oxygen.

TABLE 1

Determination of Gases in Molybdenum (in weight %)

Sample No. 1			Sample No. 2		
Hydrogen	Nitrogen	Oxygen	Hydrogen	Nitrogen	Oxygen
$6.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$5.3 \cdot 10^{-3}$	$5.4 \cdot 10^{-4}$	$0.5 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
$6.2 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	$6.2 \cdot 10^{-4}$	$0.7 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
$6.0 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	$7.7 \cdot 10^{-4}$	$0.7 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
$4.4 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$	$5.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$2.4 \cdot 10^{-3}$
$4.9 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$7.5 \cdot 10^{-4}$	$0.9 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$
Mean value					
$5.5 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$0.8 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$

TABLE 2

Determination of Gases in Tungsten (in weight %)

Sample No. 1			Sample No. 2		
Hydrogen	Nitrogen	Oxygen	Hydrogen	Nitrogen	Oxygen
$1.6 \cdot 10^{-4}$	$1.6 \cdot 10^{-3}$	$5.4 \cdot 10^{-3}$	$4.3 \cdot 10^{-4}$	$0.8 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
$1.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$3.0 \cdot 10^{-4}$	$0.4 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$
$1.9 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	$4.5 \cdot 10^{-3}$	$6.7 \cdot 10^{-4}$	$0.6 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$
$1.7 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$3.8 \cdot 10^{-3}$	$6.5 \cdot 10^{-4}$	$0.3 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$
$1.5 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$	$4.5 \cdot 10^{-4}$	$0.8 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$
Mean value					
$1.6 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	$5.0 \cdot 10^{-4}$	$0.6 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$

Two samples of molybdenum, two samples of tungsten, and three samples of niobium were analyzed. The results obtained are given in Tabes 1–3.

Experiments were carried out to establish the completeness of removal of the gases from the samples. First it was shown that the amount of extracted gases remains practically constant on increasing the temperature from 1650 to 1800°. As for oxygen and nitrogen, completeness of their removal under the conditions chosen was demonstrated on samples with known contents. For this purpose a hole (1.5 mm in diameter and 3 mm deep) was bored in a cube of molybdenum and 1–2 mg of molybdenum oxide MoO_3, tungsten oxide WO_3, or niobium oxide Nb_2O_5, placed in it; the hole was then stoppered with a molybdenum plug. The sample was analyzed by the usual method. These experiments were carried out for each metal. Particular attention was given to the completeness of removal of oxygen and nitrogen from niobium.

TABLE 3

Determination of Gases in Niobium (in weight %)

Sample No. 1			Sample No. 2			Sample No. 3		
Hydrogen	Nitrogen	Oxygen	Hydrogen	Nitrogen	Oxygen	Hydrogen	Nitrogen	Oxygen
—	—	$1.2\cdot10^{-3}$	$4.5\cdot10^{-3}$	$0.8\cdot10^{-2}$	0.29	$4.0\cdot10^{-4}$	$4.5\cdot10^{-4}$	$2.4\cdot10^{-3}$
—	—	$1.5\cdot10^{-3}$	$4.7\cdot10^{-3}$	$0.9\cdot10^{-2}$	0.38	$5.7\cdot10^{-4}$	$3.0\cdot10^{-4}$	$2.2\cdot10^{-3}$
—	—	$1.0\cdot10^{-3}$	$5.8\cdot10^{-3}$	$2.0\cdot10^{-2}$	0.30	$6.5\cdot10^{-4}$	$3.0\cdot10^{-4}$	$1.6\cdot10^{-3}$
Mean Value								
—	—	$1.2\cdot10^{-3}$	$5.0\cdot10^{-3}$	$1.2\cdot10^{-2}$	0.32	$5.4\cdot10^{-4}$	$3.5\cdot10^{-4}$	$2.0\cdot10^{-3}$

TABLE 4

Analysis of Samples of Molybdenum, Tungsten, and Niobium with Known Amounts of Oxygen (in weight %)

Molybdenum		Tungsten		Niobium	
Introduced	Found	Introduced	Found	Introduced	Found
$2.2\cdot10^{-2}$	$2.0\cdot10^{-2}$	$2.9\cdot10^{-2}$	$2.4\cdot10^{-2}$	$2.0\cdot10^{-2}$	$1.5\cdot10^{-2}$
$3.8\cdot10^{-2}$	$4.0\cdot10^{-2}$	$3.1\cdot10^{-2}$	$3.2\cdot10^{-2}$	$2.6\cdot10^{-2}$	$4.6\cdot10^{-2}$
				$4.0\cdot10^{-2}$	$2.4\cdot10^{-2}$
				$2.5\cdot10^{-2}$	$3.1\cdot10^{-2}$

Complete removal of nitrogen was only checked in the case of molybdenum and niobium, since we had no samples of tungsten nitrides at our disposal. The molybdenum powder introduced into the molybdenum cube contained 5% nitrogen while the niobium powder contained 2.7%. The results of these experiments which are given in Table 5 showed that the nitrides of molybdenum and niobium, just like the oxides, decompose completely under the experimental conditions used.

In view of the similarity in the properties of the nitrides of molybdenum and tungsten one might expect that tungsten nitrides should also decompose completely under the experimental conditions used.

TABLE 5

Analysis of Samples of Niobium and Molybdenum Containing Known Amounts of Nitrogen (in weight %)

Niobium		Molybdenum	
Introduced	Found	Introduced	Found
$2.9\cdot10^{-3}$	$3.0\cdot1^{-3}$	$4.3\cdot10^{-2}$	$4.5\cdot10^{-2}$
$8.0\cdot1^{-3}$	$7.0\cdot1^{-3}$	$6.1\cdot10^{-2}$	$7.5\cdot10^{-3}$
$1.25\cdot10^{-2}$	$1.0\cdot10^{-2}$		

Carrying out the extraction at elevated temperatures did not lead to an increase in the amount of gas extracted either.

It should be noted that in order to get complete removal of gases, it is necessary to immerse the sample completely in the iron bath (the sample is observed through a mirror fitted on the top of the oven).

Analysis of samples differing in weight showed that the amount of gas liberated is proportional to sample weight; i.e., the gas is sorbed through the whole volume.

The reproducibility is demonstrated taking Sample No. 1 for molybdenum and Sample No. 3 for niobium (Tables 6 and 7) as examples.

TABLE 6

Repeated Determination of Nitrogen and Oxygen in One Sample of Molybdenum

Experimental number	Nitrogen in % weight × 10^{-3}	Oxygen in % weight × 10^{-3}
1	1.3	6.7
2	1.1	5.6
3	1.7	5.1
4	1.5	5.3
5	1.8	4.4
6	1.6	5.0
7	1.3	5.1
8	1.1	7.5
9	1.4	5.1
10	1.3	4.6

Mean value

$(1.4 + 0.25) \cdot 10^{-3}\ \%$ $(5.5 \pm 0.9) \cdot 10^{-3}\ \%$

Mean square error

| ± 14% | ± 16%

TABLE 7

Repeated Determination of Hydrogen, Nitrogen, and Oxygen in One Sample of Niobium

Experimental number	Hydrogen in % weight × 10^{-4}	Nitrogen in % weight × 10^{-4}	Oxygen in % weight × 10^{-3}
1	4.0	4.5	2.4
2	5.7	3.0	2.2
3	5.5	3.0	1.6
4	5.7	3.8	1.1
5	5.1	3.0	1.0
6	6.0	6.0	1.3
7	4.2	4.1	2.6
8	4.3	4.4	1.9
9	4.3	4.1	1.6
10	5.0	3.2	1.3
11	5.2	4.9	3.0

Mean value

$(5.0 \pm 0.7) \cdot 10^{-4}\%$ $(4.0 \pm 0.8) \cdot 10^{-4}\%$ $(1.8 \pm 0.6) \cdot$
$\cdot 10^{-4}\%$

Mean square error

| ±14% | ±20% | ±33%

The method developed allows one to determine the gas content of molybdenum, tungsten, and niobium with the following sensitivities:

Hydrogen – $1 \cdot 10^{-4}\%$; nitrogen – $1 \cdot 10^{-3}\%$; oxygen – $1 \cdot 10^{-3}\%$.

SUMMARY

The vacuum fusion method with an iron bath is used for determination of oxygen, hydrogen, and nitrogen in molybdenum, tungsten, and niobium; the apparatus used was one constructed at the Institute of Geochemistry and Analytical Chemistry.

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PHOTOMETRIC DETERMINATION OF TUNGSTEN AND MOLYBDENUM AS THEIR THIOCYANATE COMPLEXES

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The most widely used methods for determining tungsten and molybdenum photometrically are based on formation of colored thiocyanate complexes. In contrast to the thiocyanate complexes of iron, cobalt, bismuth, and other metals, the colored compounds of tungsten and molybdenum are only formed in the presence of a reducing agent. All the same the effect of various reducing agents on the compounds of sexivalent molybdenum and tungsten in the presence of thiocyanate (in acid media) has not been studied enough. Quinquevalent molybdenum gives the most intensely colored compound [1-3]. Sexivalent molybdenum is usually reduced by stannous chloride, iodide solution, etc. A considerable excess of freshly prepared stannous chloride leads to an appreciable weakening of the color of molybdenum thiocyanate complexes [1]. Stronger reducing agents such as titanium trichloride lead to formation of even less intensely colored molybdenum compounds. Under the action of strong reducing agents, molybdenum in certain amounts does not interfere with photometric determination of tungsten [4,5]. Thus the effect of the nature of the reducing agent is significant for the determination of molybdenum and tungsten, particularly in the presence of molybdenum. The relation between the character and intensity of the color of the thiocyanate compounds of molybdenum and tungsten and the valency of the latter cannot be established on the basis of the values of the oxidation potentials. The oxidation potentials for the various valency states of tungsten and molybdenum, and also for various reducing agents, alter in the presence of thiocyanates.

The problem which forms the subject of this article was a study of the light absorption of the thiocyanate complexes of molybdenum and tungsten in relation to the valency of the central atoms, from the point of view of the photometric determination of these elements.

For each element independently (tungsten and molybdenum) two series of tests were carried out. In one series of tests, various amounts of a strong reducing agent were added to a known amount of an acid solution of molybdate and tungstate respectively, so as to prepare tungsten and molybdenum in various states of reduction. Experiments of this type on the study of the action of various reducing agents are of immediate interest for photometric determination. All the same, conclusions drawn regarding the valency of tungsten and molybdenum cannot be regarded as fully substantiated. Part of the reducing agent added may not react with tungsten or molybdenum as a result of disparity between the values of the oxidizing agent and reducing agent under actual conditions. In this connection therefore a second series of test was carried out for each element (tungsten or molybdenum). The original solutions in this series of experiments were solutions of sexivalent and trivalent molybdenum (and similar ones in the case of tungsten). By mixing various valumes of these solutions it was possible to prepare a series of solutions with a different mean valency state for molybdenum or tungsten at an equal total concentration of each element. Thus, the series of solutions was of equal molarity with respect to the total concentration of molybdenum or tungsten, but differed with respect to the value of the mean valency.

The value of the mean valency of molybdenum or tungsten could be controlled each time by titration of separate aliquots of the solution with dichromate. This determination was made before addition of thiocyanate, since the latter can be oxidized by dichromate. Tests showed that the curves relating optical density of the solution to the mean valency of molybdenum or tungsten practically coincide both during reduction with trivalent titanium or with divalent chromium and during mixing of the corresponding amounts of trivalent and sexivalent molybdenum or tungsten.

The Relation Between Optical Density of the Solution and the Valency of Tungsten in the Thiocyanate Complex

Experiments were carried out in hydrochloric acid media (2-4 N), in the presence of a large excess of ammonium thiocyanate (1.0 mole), for a constant concentration of tungsten used in the form of potassium tungstate (2×10^{-3} g.mole/liter). Various amounts of solutions of titanium trichloride or divalent chromium were used for reduction. The optical density of a series of solutions such as this was measured on a Pulfrich photometer using light filters with maximum transmission in the region 470 and 430 mμ respectively; the layer thickness was 2 mm.

The reducing agents were prepared beforehand and their concentration established titrimetrically with potassium permanganate. Divalent chromium solution was prepared by reducing chrome alum with zinc amalgam. A solution of trivalent titanium was prepared by reducing a solution of quadrivalent titanium with zinc amalgam. In order to exclude the possibility of partial oxidation by atmospheric oxygen during the tests, the solutions were mixed in a carbon dioxide atmosphere. The results of these experiments are shown in Fig.1.

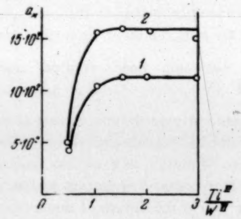
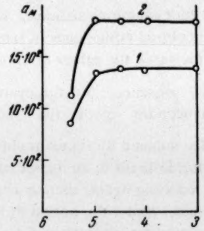


Fig. 1. Relation for the molar extinction coefficient of the thiocyanate compounds of tungsten during reduction with titanium trichloride. The amount of reducing agent in g. equivalents per g. atom of tungsten is plotted on the abscissa, while the molar extinction coefficient (a_M) is plotted along the ordinate:
Curve 1) at λ = 470 mμ; 2) at λ = = 430 mμ.



Mean valency of tungsten

Fig. 2. Relation for the molar extinction coefficient of the thiocyanate compounds of tungsten during mixing of solution of W^{VI} and W^{III}. The mean valency of tungsten is plotted along the abscissa while the molar extinction coefficient is plotted along the ordinate:
Curve 1) at λ = 470 mμ; 2) at λ = = 430 mμ.

From a consideration of the curves, it is evident that after addition of 1 g. equivalent of reducing agent to 1 g of sexivalent tungsten, the optical density of the solution does not change further. This indicates that tungsten in valency states lower than five forms complexes whose optical density is similar to that for quinquevalent tungsten.

In order to confirm the conclusions regarding the relation between optical density and the valency of tungsten in thiocyanate complexes, we replaced divalent chromium and trivalent titanium by a solution of trivalent tungsten as indicated above. The remaining conditions were the same as for the first series. Thus, in this series of tests, the total tungsten concentration was constant, and only the mean valency was altered. The results of these experiments are given in Fig. 2.

A comparison of Figs. 1 and 2 shows that the absolute values of the light absorption of solutions in the second series is somewhat higher; presumably this is the result of somewhat incomplete reduction of tungsten by trivalent titanium under the given conditions. Nevertheless, the general relation between optical density of solutions of the thiocyanate complexes of tungsten, and the valency state of the latter, is the same in both series. It is obvious that in order to determine tungsten photometrically, it is essential to reduce it to the quinquevalent state, while further reduction of tungsten has no effect on its light absorption.

Relation Between Optical Density of the Solution and the Valency of Molybdenum in Its Thiocyanate Complex

Light absorption was carried out in hydrochloric acid media (1 - 2 N) at a constant molybdenum concentration of $2 \cdot 10^{-3}$ g.mole/liter, and for various amounts of divalent chromium and trivalent titanium respectively; the concentration of ammonium thiocyanate in these solutions was 1.0 M.

The original solutions of potassium molybdate and reducing agent were mixed in a carbon dioxide atmosphere in various proportions, viz: to 1 g atom of sexivalent molybdenum was added from 0.5 to 3 g equivalents and more of reducing agent. Optical density was measured at 500, 470, and 430 mμ. The results are given in Fig. 3. The curves were constructed on the basis of results of a series of experiments in which trivalent titanium was used as reducing agent; similar results were also obtained for solutions in which divalent chromium was used as reducing agent.

Maximum color intensity was observed on adding 1g ion of reducing agent to 1 g atom of sexivalent molybdenum; this corresponds to the formation of a colored compound with quinquevalent molybdenum. Further addition of reducing agent led to gradual decolorization of the solution. Thus, in the presence of a large excess of reducing agent, weakly colored thiocyanate complexes of molybdenum are formed. The molar absorption coefficient of the latter is approximately a sixth of that of the most intensely colored thiocyanate complex of quinquevalent molybdenum.

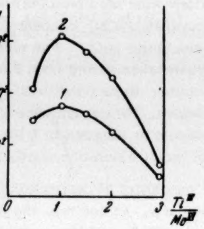


Fig. 3. Relation for the molar extinction coefficient of the thiocyanate complexes of molybdenum during reduction with titanium trichloride. The amount of reducing agent in g. equivalents per g. atom of molybdenum is plotted along the abscissa.

Curve 1) at λ = 500 mμ; 2) at λ = = 430 mμ.

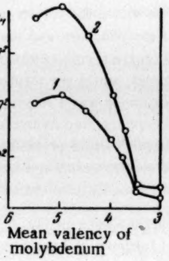


Fig.4. Relation for the molar extinction coefficient during mixing of solutions of Mo^{VI} and Mo^{III}:

Curve 1) at λ = 500 mμ; 2) at λ = = 430 mμ.

The relation between the color of the solution and the valency of molybdenum in its thiocyanate compounds was also studied in a series of experiments, under similar conditions, with the difference that a solution of trivalent molybdenum was used as the second component. The latter was prepared by reducing some of the potassium molybdate solution originally used with zinc amalgam. Test solutions of sexivalent and trivalent molybdenum were mixed so that the total concentration of molybdenum through the series was constant, only the mean valency state of the molybdenum being altered. Results are shown in Fig. 4.

Thus, during photometric determination of molybdenum, choice of reducing agent and reduction conditions is of primary importance. The use of such strong reducing agents as solutions of trivalent titanium or divalent chromium in acid media leads to formation of weakly colored molybdenum thiocyanate complexes, with very weak absorption at 470 and 430 mμ. The color of the thiocyanate compounds of tungsten on the other hand, as already pointed out, does not alter on addition of excess of the reducing agents mentioned.

Photometric Determination of Molybdenum and Tungsten when Present Simultaneously

The colored thiocyanate compounds of molybdenum and tungsten are formed under similar conditions, on addition of thiocyanate and reducing agent. Accordingly, the effect of test conditions on the photometric determination of these elements when present together is of great importance for the analysis of various materials [4 -8].

The thiocyanate compounds of molybdenum and tungsten differ with respect to their absorption spectra, their stability, and their behavior towards reducing agents. Accordingly, within certain limits, it is possible to determine one of them in the presence of the other. In a general sense the relationship is fairly complicated, since molybdenum and tungsten both form a series of thiocyanate compounds depending on a concentration, and on the excess of thiocyanate ions. Each compound is characterized by different behavior towards reducing agents, in accordance with the normal potential of the latter, and even in accordance with their concentration. Finally, the absorption spectra of the individual compounds differ with respect to the value of their molar extinction coefficients and, sometimes, even with respect to the position of their maxima. Nevertheless, despite the complex character of the relationship, it is possible to find some general approach whereby optimum conditions can be attained.

Choice of Spectral Region for Measuring the Optical Density of the Solution.

In Fig. 5 are shown the results of tests carried out on measurement of the optical density of the thiocyanate compounds of molybdenum and tungsten, in which various light filters were used on a Pulfrich photometer. Molybdenum and tungsten concentration was $5 \cdot 10^{-4}$ moles/ liter, thiocyanate $[SCN]^-$ concentration was varied from 0.6 to 1.0 moles, while the solutions were 1-2 M with respect to hydrochloric acid. The reducing agent in this series of experiments was a solution of stannous chloride, the amounts taken varied from 0.5 to 1.0 ml of a 20% solution in concentrated hydrochloric acid per 10 ml of total volume; these conditions approximate those recommended in various procedures for determination of molybdenum. For convenience in comparing the results, all the results were expressed in terms of 1 g ion of molybdenum or tungsten in 1 liter and for a layer thickness of 1 cm; i.e., the optical density is given in the form of molar absorption coefficients (a_M).

From the curves shown in Fig. 5 it is evident that there exists a possibility of determining molybdenum in the presence of tungsten as long as optical density is measured at 500 mμ. At 436 mμ the light absorption of the thiocyanate compounds of molybdenum and tungsten is almost identical; at 465 mμ the light absorption of the thiocyanate compounds of tungsten is approximately half of that for the molybdenum compounds, while at longer wavelengths the difference increases. At 496 mμ, the ratio of the values of a_M at 0.6 molar concentration of the thiocyanate amounts to $a_{M-Mo} : a_{M-W} = 3700 : 140$; i.e. one is about 25 times the other.

The accuracy with which optical density is measured under normal conditions in photometric determination amounts to 2 -4% of the value being measured. Consequently, under the conditions outlined above, the presence of twice its weight of tungsten will not affect the determination of molybdenum, since such an amount of tungsten will only increase the optical density by 2 - 4%. Determination of tungsten in the presence of molybdenum is only possible when the optical density is measured in the ultraviolet (Fig. 5).

Effect of Thiocyanate Concentration. The colored thiocyanate compounds of molybdenum and tungsten are characterized by different stability, those of molybdenum being the most stable. In accordance with this fact, molybdenum forms a thiocyanate complex at a lower thiocyanate concentration. Half of the total amount of quinquevalent molybdenum is transformed into the colored compound $Mo(SCN)_5$ at $[SCN^-] = 0.08$ mole [3]. In Fig. 6 are given results for measurements of optical density at 465 mμ. Similar results are given in Fig. 7 for the optical density at 436 mμ.

The results given in Figs. 6 and 7 show that molybdenum is practically completely complexed as a colored thiocyanate compound at a concentration of $[SCN]^- \geq 0.3$ mole. At concentrations of $[SCN]^- > 0.6$ formation of the less intensely colored molybdenum starts. Thus, in order to determine it, it is best to adjust the thiocyanate concentration to the range 0.3 - 0.6 mole (in the final volume of solution). Under such conditions maximum sensitivity is achieved, while small variations in the thiocyanate concentration do not show any essential effect on the experimental results; at the same time, it is evident from Figs. 6 and 7 that the thiocyanate concentration should be the same in test and standard solutions.

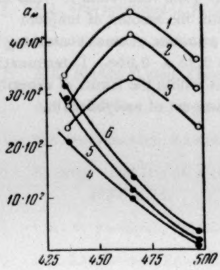


Fig. 5. Relation between the light absorption of the thiocyanate compounds of molybdenum (Curves 1, 2, and 3), and tungsten (Curves 4, 5, and 6), and wave length (in mμ):
1 and 4 at [SCN]$^-$ concentration of 0.6 mole; 2 and 5 at [SCN]$^-$ concentration of 0.75 mole; and 3 and 6 at [SCN]$^-$ concentration of 1.0 mole/liter respectively.

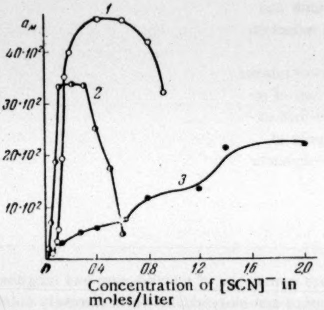


Fig.6. Relation between the light absorption of thiocyanate compound and thiocyanate concentration during reduction with stannous chloride, at 465 mμ.
1) for molybdenum thiocyanate complexes in the presence of an 800-fold excess of reducing agent; 2) ditto for a 2000-fold excess of stannous chloride with respect to molybdenum; 3) for tungsten thiocyanate compounds

Curve 3 in Figs. 6 and 7 shows that at a thiocyanate concentration of 0.3 – 0.6 mole, the tungsten in solution only starts to form its thiocyanate complex. Thus in order to determine molybdenum photometrically in the presence of tungsten it is best to adjust the potassium or ammonium thiocyanate concentration to low values. The favorable effect of a low thiocynate concentration is also evident from Fig. 5.

Decreasing thiocyanate concentration below 0.3 mole decreases the sensitivity and reproducibility of the reaction for molybdenum as is obvious from what was said above. Furthermore, decreasing the thiocyanate concentration in itself (without making use of differences in absorption spectra) does not enable one to eliminate the effect of tungsten on molybdenum determination. Actually, by comparing the light absorption of the thiocyanate compounds of tungsten at [SCN]$^-$ = 0.3 and 2.0 mole, it is clear (Fig. 6 and 7) that even at low thiocyanate concentrations 20 – 30% of the tungsten is already present in the form of the colored thiocyanate compound.

For determining tungsten in the presence of molybdenum it is expedient to increase the concentration of thiocyanate ions as much as possible (see Figs. 6 and 7).

Practically complete complexing of tungsten as the colored compound is observed on increasing thiocyanate concentration to 1.5 mole. Under these conditions the less intensely colored molybdenum thiocyanate compound is formed so that the effect of molybdenum on tungsten determination is decreased.

It was shown above that for the determination of tungsten in the presence of molybdenum, the behavior of the two elements toward reducing agents is very important. Curves 1 and 2 in Fig. 6 (and the same curves in Fig. 7) show that excess stannous chloride, under all conditions, leads to a weakening of color intensity of solutions of molybdenum thiocyanate complexes. Under the conditions used for the determinations, this effect is sometimes less appreciable because of the high concentration of trivalent iron in the test solution. The latter reacts with divalent tin, and a considerable amount of quadrivalent tin is formed. This increases the oxidation potential of the system Sn^{IV}/Sn^{II}, and thus decreases the reducing capacity of divalent tin. Nevertheless, the use of stannous chloride leads to less reproducible results; accordingly it is better to use other reducing agents which are weaker than stannous chloride for determining molybdenum, such a reducing agent is thiourea which was recommended by Zaichikova [8]. At the same time, sufficiently strong reducing agents, whether iron is present or not, as indicated above, lead to the formation of the weakly colored thiocyanate compounds of molybdenum with a valency of less than five. Thus, excess of thiocyanate ions and reducing agent (Fig. 6 and 7) allow one to determine tungsten photometrically in the presence of molybdenum.

When the conditions mentioned above are observed, it is possible to determine tungsten photometrically in the presence of equal and even greater amounts of molybdenum than itself (and vice-versa). Thus in a sample of fast cutting steel containing 4.08% tungsten and 0.08% molybdenum, the amount of tungsten found was 4.07 ± 0.05% (using titanium trichloride as reducing agent). In a sample of steel containing 2.74% tungsten and 2.61% molybdenum, the amount of tungsten actually found was 2.75 ± 0.05%. Determination of tungsten in a colorimeter (without a light filter) gives a result which is within the limits of experimental error for optical density (± 3% relative) in the presence of three times its amount of molybdenum.

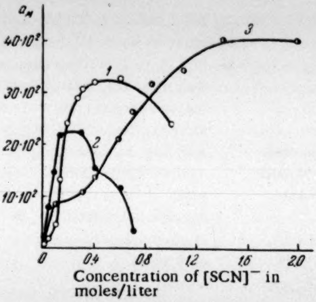


Fig. 7. Relation between the light absorption at 436 mμ of thiocyanate compounds and thiocyanate concentration during reduction with stannous chloride.

1) for molybdenum thiocyanate complexes in the presence of an 800-fold excess of reducing agent; 2) ditto for a 2000-fold excess of stannous chloride with respect to molybdenum; 3) for tungsten thiocyanate compounds.

SUMMARY

1. The relation between optical density of the thiocyanate complexes of molybdenum and tungsten and the valency states of these metals has been studied. Both tungsten and molybdenum form intensely colored complexes on being reduced to the quinquevalent state. On further reduction to the trivalent state, the light absorption of the thiocyanate complexes of tungsten hardly changes at all. At the same time the light absorption of the thiocyanate complexes of molybdenum decreases strongly on being reduced to a valency state lower than five. The significance of these results has been discussed in relation to the photometric determination of molybdenum, and in relation to decreasing the influence of molybdenum on tungsten determination.

2. The light absorption of the thiocyanate complexes of molybdenum and tungsten has been studied in relation to wave length, and also to thiocyanate ion concentration. It has been shown that in order to weaken the effect of tungsten on molybdenum determination it is advisable to measure the optical density at 500 mμ, at which wavelength tungsten exhibits very little absorption. For this purpose it is also advisable to lower the thiocyanate concentration since, under such conditions, the percentage of tungsten complexed as the colored compound decreases. All the same, the thiocyanate concentration should not be lowered below 0.3 mole; otherwise the amount of molybdenum which is complexed also decreases.

In order to cut down on the effect of molybdenum on tungsten determination, it is expedient to increase thiocyanate concentration to 1.5 mole and higher, and also to add excess strong reducing agent and measure light absorption in the shortest possible wave length region.

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STUDIES ON THE EXTRACTION OF NIOBIUM THIOCYANATE COMPLEXES WITH ORGANIC SOLVENTS BY MEANS OF THE RADIOACTIVE ISOTOPE Nb^{95}

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Determination of niobium as a thiocyanate complex by a photometric method has been fairly widely used in recent years [1 - 3]. It has been known for a long time that on adding potassium thiocyanate, metallic zinc, and hydrochloric acid to a solution of a niobium salt, a yellow color develops [4]. The reaction has been studied by quite a few research workers [5 - 6]. In 1942 Monyakova and Fedorov [7] used this reaction of formation of a thiocyanate complex for determining niobium in various materials.

As a result of a study of the products formed on combining the thiocyanate complex of niobium with various alkaloids (quinine, cinchonine, etc), Alimarin and Podvalna gave it the formula $H[NbO(SCN)_4]$. The thiocyanate complex forms a compound with the formula $H_2[NbO\ O(C_2H_5)_2(SCN)_4]$. with diethyl ether. Only in the presence of free HSCN, which is readily soluble in diethyl ether, are the thiocyanate complexes of niobium sufficiently stable in ether solution.

The yellow color of the complex is more stable in ether solution than in aqueous solution.

A study of the extraction of the niobium thiocyanate complex with diethyl ether shows that niobium only passes partially into the ether layer, despite the fact that under these conditions, the aqueous layer becomes colorless. Repeated extraction does not lead to complete transfer of niobium into the ether layer. It is obvious that some of the niobium must be present in the form of a compound which is not extractable with ether. It has, however, been established that the intensity of the color of the ether solution remains constant after the first extraction, so that it is possible to carry out a quantitative determination of niobium by a photometric method [1].

We have studied extraction of micro-amounts of niobium by means of the radioactive isotope Nb^{95} (half-life period 37 days, β-ray energy 0.15 mev).

The following procedure was adopted for studying the extraction of the thiocyanate complex of niobium: into a graduated 10 ml test tube fitted with a ground glass stopper was measured 1 ml of a solution containing the radioactive indicator Nb^{95} plus carrier (100 γ Nb); this was followed by 2.5 ml of 20% KSCN. After the solutions had been carefully shaken, 1.5 ml of 15% $SnCl_2$ solution in 4 N HCl was added and the whole mixture agitated again. 2.5 ml of concentrated HCl was next added and the shaking operation repeated [3]. This solution was kept for 45 minutes at 18 - 20°, and then solvent was added in such amount (diethyl ether and other solvents) that after shaking the solution (100 times) the ratio of the volumes of the two phases was 3:1.

Radioactive niobium was purified as follows: to 10 mg of niobium as K_2NbF_7 was added a solution of sulfuric and citric acids, the radioactive indicator solution Nb^{95} was then added (without carrier) and the niobium precipitated with cupferron. The filtered deposit of niobium cupferronate was washed several times with sulfuric acid and water. After calcining the precipitate, an aliquot of the Nb_2O_5 was fused with $K_2S_2O_7$ in an electric muffle. The melt was dissolved in a dilute solution of tartaric acid, and water was added to bring the concentration to 100 γ Nb/ ml.

The first factor to be studied was the effect of time of standing of the solution before extraction on the completeness of extraction of niobium with diethyl ether (Fig. 1).

Percentage extraction of niobium does not change on increasing the time of standing before extraction. Only after 7 hours standing is there observed a significant drop in the percentage of niobium extracted by ether (a drop down to 57.9%).

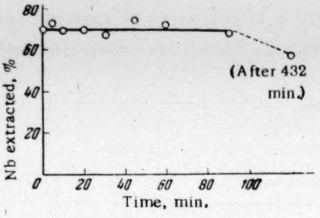


Fig.1. Effect of time of standing of solution before extraction on percentage extraction of niobium with diethyl ether.

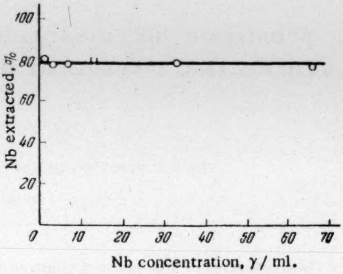


Fig. 2. Effect of niobium concentration on its percentage extraction by diethyl ether.

In the next series of experiments we studied the effect of niobium concentration on its percentage extraction with diethyl ether (Figs. 2 and 3). The results of these experiments show that on changing the niobium concentration over a wide range (from $1.3 \cdot 10^{-5}$ to 66 γ/ ml as Nb), the percentage of niobium changed very little (75 – 80%). Even when Nb^{95} was used without a carrier, the ether extracted 78.8%.

At concentrations of 1.3 γ Nb/ ml and lower in the original solution, the color of the ether layer was so weak that colorimetric determination was out of the question.

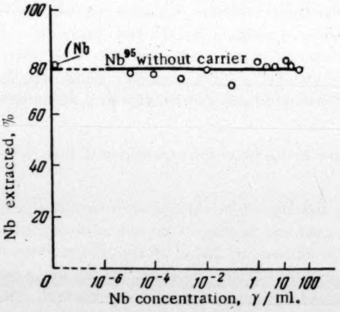


Fig. 3. Effect of ultra-small concentration of niobium on its percentage extraction by diethyl ether.

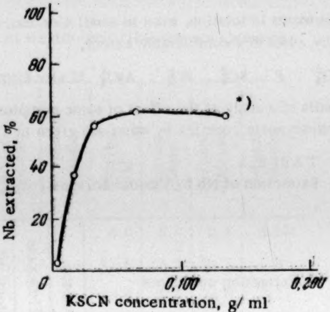
Niobium was not extracted at all by ether if no potassium thiocyanate was added. On addition of small amounts of KSCN there was a sharp increase in extraction of niobium. At concentration of 0.05 – 0.6 g KSCN/ ml up to 60% of Nb was extracted, while on further increasing KSCN concentration to 0.100 – 0.130 g/ ml, percentage extraction of niobium did not alter. Thus only the thiocyanate complex of niobium goes over into the ether layer.

At very low concentrations of KSCN in solution (0.003 – 0.0003 g/ ml), both aqueous and ether layers were completely colorless, and only 0.5 – 2.5% of niobium was extracted. At KSCN concentration of 0.017 – 0.033 g KSCN/ ml, the comparatively weak color of the yellow thiocyanate complex appeared in the aqueous phase, although the percentage extraction of niobium by the ether layer reached comparatively high values (36.6 – 56%). It may be postulated that under these conditions, some of the niobium is extracted by ether as a colorless thiocyanate complex.

In Fig. 4 is shown the relation between percentage niobium extraction and concentration of KSCN in solution. Maximum extraction was observed at a concentration of 0.02 – 0.03 g KSCN/ ml; there was no increase in percentage extraction of niobium on increasing the KSCN concentration further.

During a study of the effect of hydrochloric acid concentration on percentage extraction of the thiocyanate complex of niobium, it was established that on changing HCl concentration within the fairly wide limits of 0.03 - 0.265 g/ ml, percentage niobium extraction changed very little(Fig.5). At low HCl concentrations in the solution (0.03 - 0.06 g/ ml) the aqueous solution remained colorless before extraction; nevertheless, after extraction, the ether layer acquired a yellow color and percentage niobium extraction reached a normal value. On lowering HCl concentration in solution, the color of the hydrochloric solution before extraction weakened significantly.

At high HCl concentrations, the aqueous layer acquire an orange-yellow color.



*) A small amount of salt was deposited.

Fig. 4. Effect of KSCN concentration on extraction of niobium by diethyl ether.

Niobium can be extracted from solution as the hydrochloric complex [8 - 10]. As a result of our experiments, it was established that niobium was very poorly extracted from hydrochloric solutions (0.3 - 2%); consequently the part played by this process during extraction of the thiocyanate complex is very small. $SnCl_2$ concentration had very little effect on extraction of niobium by ether. Even when no $SnCl_2$ was added, the solution had a yellow color, while the percentage niobium extracted reached a considerable value.

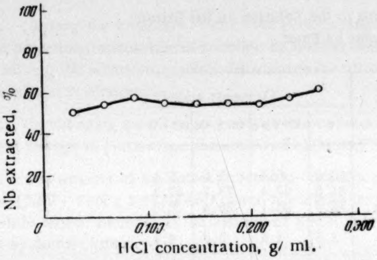


Fig. 5. Effect of HCl concentration on extraction of niobium by ether.

In Table 1 a comparison is made of the results of experiments carried out on extraction of the thiocyanate complex of niobium with various organic solvents. These experiments show that benzene, cyclohexane, chloroform, and carbon tetrachloride hardly extract niobium at all. Diethyl ether only extracts 65% of the niobium. Higher extraction figures were given by the following solvents: cyclohexanone (70.6%), methyl butyl ketone (71.3%), isoamyl alcohol (72.7%), ethyl acetate (72.7%), amyl acetate (74.3%), and isopropyl ether (75.4%). The highest result was obtained with butyl alcohol (89.4%); accordingly, the latter is recommended for extracting the thiocyanate complex of niobium.

During extraction of niobium with benzene, cyclohexane, chloroform, and carbon tetrachloride, the layer of the extractant remained colorless while the aqueous layer retained a yellow color.

In using butyl alcohol, cyclohexanone, and methyl butyl ketone, the extractant was yellow, while the aqueous layer became colorless and turbid as a result of the formation of an emulsion with the solvent. During extraction of niobium with isoamyl alcohol, diethyl ether, ethyl acetate, and amyl acetate, the layer of the extractant had a yellow color, while the aqueous layer became colorless. Good results were obtained on extracting with alcohols (butyl), ethers, and esters, and also with ketones.

In order to prevent formation of colored thiocyanate complexes of iron, $SnCl_2$ is usually added to the solution to reduce Fe^{3+} to Fe^{2+}; accordingly, small amounts of iron should not interfere with the photometric determination of niobium.

In Table 2 are given the results of a study of the effect of elements which form colored, extractable thiocyanate complexes (Fe^{3+}, Co, W) on extraction of niobium. These results show that the presence of certain elements in solution, even in small amounts, can suppress the extraction of the niobium thiocyanate complex by ether to a considerable extent.

$C_2O_4^{2-}$, F^-, SO_4^{2-}, PO_4^{3-}, AsO_4^{3-} hinder formation of the yellow niobium thiocyanate complex.

Results of a study of the effect of some complexing agents (tartrates, oxalates, etc) on extraction of the niobium thiocyanate complex by ether are given in Table 3.

TABLE 1

Extraction of Nb by Various Solvents (in %)

Extraction conditions	Benzene	Cyclohexane	Chloroform	Carbon tetrachloride	Butyl alcohol	Isoamyl alcohol	Ethyl ether	Isopropyl ether	Ethyl acetate	Amyl acetate	Methyl butyl ketone	Cyclohexanone
Distribution coefficient K	—	—	—	—	21.3	7.0	5.5	8.1	10.7	7.4	6.4	6.8
Percentage extraction for Nb	0.0	0.0	0.0	0.0	89.4	72.7	65.0	75.4	72.7	74.3	71.3	70.6
Nb concentration in solvent layer in γ/ ml	—	—	—	—	31.9	26.0	26.0	27.4	36.3	26.6	25.5	27.1
Nb concentration in hydrochloric acid solution in γ/ ml	—	—	—	—	1.5	3.7	4.7	3.4	3.4	3.6	4.0	4.0

TABLE 2

Effecto of Addition of Certain Elements to the Solution on the Extraction of Niobium Thiocyanate Complexes by Ether

Extraction conditions	Elements added			
	0	100 γ Fe	100 γ Co	100 γ W
Distribution coefficient K	13.0	6.4	7.9	6.4
Percentage extraction of Nb	81.6	67.4	73.7	67.2
Nb concentration in the ether layer in γ/ ml.	32.6	28.1	28.4	28.0
Nb concentration in the hydrochloric acid solution in γ/ ml	2.5	4.4	3.6	4.4

Acid sodium phosphate or ascorbic acid had little effect on extraction of the niobium thiocynate complex (79 – 74%), but the color weakened. Sodium citrate, tartrate, and sulfate respectively, as well as sodium arsenate, depressed the percentage niobium extracted by ether appreciably (55 – 68%). In the presence of sodium fluoride only a small amount of niobium (5.6%) was extracted; in this case both the aqueous and ether layers remained colorless.

Addition of sodium oxalate or ammonium oxalate completely suppressed formation of the niobium thiocyanate complex; the solution remained completely colorless and no niobium was extracted by the ether.

In the next series of experiments the yellow colored ether solution of the niobium thiocyanate complex was mixed with ethyl alcohol. The solution was gradually evaporated on a water bath. After some time the yellow alcohol solution was cooled with cold water and precipitate separated out. The yellow saturated solution was evaporated to dryness and its content of niobium determined. After several crystallizations a colorless salt was obtained which did not contain any niobium. All the niobium was concentrated in the yellow alcohol solution. Thus, it can be concluded that niobium is found in solution as a colorless or yellow thiocyanate complex. It is possible that these two complexes may occur simultaneously in solution; one colored yellow, the other colorless, depending on conditions.

TABLE 3

Effect of Some Complexing Agents on Extraction of the Niobium Thiocyanate Complex by Ether

Results	In the absence of complexing agent	Acid sodium phosphate (Na_2HPO_4)	Sodium citrate	Sodium tartrate	Sodium oxalate	Ammonium oxalate	Ascorbic acid	Sodium sulfate	Sodium arsenate	Sodium fluoride
Distribution coefficient K	8.9	12.3	6.2	6.8	—	—	8.8	5.8	3.8	0.16
Percentage extraction of Nb	75.2	79.6	66.4	68.3	0.0	0.0	73.8	66.3	55.2	5.6
Nb concentration in the hydrochloric solution in γ/ ml	30.1	33.1	27.7	28.5	—	—	30.8	26.5	23 0	2.2
Nb concentration in the hydrochloric solution in γ/ / ml	3.4	2.7	4.5	4.2	—	—	3.5	4.6	6.0	13.4

Note: The solution being extracted contained 23-24 mg/ ml of complexing agent

Note. The solution being extracted contained 23 – 24 mg/ ml of complexing agent.

SUMMARY

1. Leaving the solution to stand over periods ranging from 1 to 90 minutes before extraction has no effect on percentage extraction of niobium by diethyl ether. If extraction with ether is carried out immediately after mixing the solutions – when the solution is still colorless – extraction of a colorless thiocyanate complex of niobium is observed.

2. On changing the niobium concentration over a wide range (from 66 to 10^{-5} γ Nb/ ml) there is no significant change in percentage extraction of niobium (71 – 80%) by diethyl ether.

3. The amount of niobium extracted is insignificant when no KSCN is added; on adding small amounts of KSCN (0.02 – 0.04 g KSCN/ ml) there is a sharp increase in the percentage extraction of niobium (up to 60%), while further increase in the amount of KSCN does not lead to an increase in percentage extraction of niobium by diethyl ether.

At low KSCN concentrations (0.017 – 0.033 g KSCN/ ml) formation of a colorless niobium thiocyanate complex is observed.

4. On changing hydrochloric acid concentration in the range 0.03 – 0.265 g HCl/ ml there is little change in percentage extraction of niobium by diethyl ether (55 – 60%). At low acid concentrations (0.03 – 0.09 g HCl/ ml) the solution before extraction remains colorless; this indicates formation of a colorless thiocyanate complex of niobium which is readily extracted by diethyl ether.

5. Niobium is extracted with ether from pure hydrochloric acid solutions to the extent of 0.3 – 1.9% (hydrochloric acid concentrations 0.15 – 0.295 g HCl/ ml).

6. Addition of $SnCl_2$ to the solution has little effect on percentage niobium extracted by diethyl ether (78-80%). When no $SnCl_2$ is added, a yellow color develops and the percentage of miobium extracted by ether changes little.

7. The thiocyanate complexes of niobium are extracted best by butyl alcohol; isopropyl ether and amyl acetate also give good results.

8. The presence in solution of some elements (Fe, W, Co), which form thiocyanate complexes, leads to a significant depression of the percentage niobium extracted by ether.

9. The effect of various complexing agents (sodium tartrate, citrate, etc) on extraction of the thiocyanate complexes of niobium by diethyl ether has been studied.

10. The optimum conditions for extraction of the thiocyanate complexes of niobium with diethyl ether are as follows: 0.06 – 0.100 g KSCN/ml; 0.100 – 0.200 g HCl/ml; 0.01 – 0.05 g $SnCl_2$/ml.

The recommended extractant is butyl alcohol.

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DETERMINATION OF NIOBIUM IN THE PRESENCE OF LARGE AMOUNTS OF TITANIUM

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The chemical analysis of minerals, ores, slags, and some materials from metallurgical production containing niobium and tantalum is, at the same time, one of the most complicated but least investigated questions in analytical chemistry. Determination of these elements is particularly difficult when test material contains large amounts of titanium and zirconium at the same time. Most published methods for separation of earth metals from zirconium and titanium are based on the greater tendency of the salts of niobium and tantalum to hydrolyze, as compared with those of titanium and zirconium, and also on the difference in solubility, or stability, of the inorganic and organic complex compounds of these elements, e.g. the fluorides, tartrates, oxalates, salicylates, and pyrogallates [1-4].

When any of the published methods are used for determining earth metals in the presence of significant amounts of titanium, the content of the latter in the precipitates of niobium and tantalum pentoxides usually amounts to several milligrams. Thus, during determination of small amounts of niobium (mg), the error obtained on introducing a correction for the titanium content into the result may be quite appreciable.

The aim of the work described here was to develop a better method for determining and separating niobium from large amounts of titanium.

With this idea in mind we studied conditions for precipitating and separating niobium from large amounts of titanium in the presence of some complexing agents (chromotropic and ascorbic acid) which can keep titanium in solution.

Chromotropic acid $(HO)_2C_{10}H_4(SO_3H)_2$ or its sodium salt $C_{10}H_6O_8S_2Na_2$ form a wine-red colored complex with Ti^{IV} in weak sulfuric acid. This complex has been studied in detail by Okach and Sommer [5]; they showed that the complex compound formed between titanium and chromotropic acid is stable at pH 3.5-5 and is suitable for photometric determination of titanium, since the color is practically stable under these conditions.

It has been established, however, that chromotropic acid is not suitable for complexing titanium during niobium determination.

Ascorbic acid $C_6H_8O_6$ forms with titanium ions a complex which, during precipitation of niobium with tannin, remains in solution. Hines and Boltz [6], have used it for the spectrophotometric determination of titanium.

To measured volumes of a standard solution of niobium in sulfuric acid – each aliquot containing 3.6 mg of niobium pentoxide – was added a standard solution of titanium, so as to get final solutions with ratios of $Nb_2O_5 : TiO_2$ of 1:30 and 1:50 respectively. To each of these solutions, after neutralization with ammonia followed by acidification with 10 ml of hydrochloric acid sp.gr.1.19, was added 2 g of ammonium chloride and 0.1 g ascorbic acid; the solutions were diluted with water to a volume of 170-180 ml and heated to 50-70°; niobium was then precipitated with a freshly prepared 1% aqueous solution of tannin. The rate of formation of the precipitate was found to depend on the concentration of both niobium and titanium in solution. The greater the amount of niobium, the more rapid was precipitate formation. On the other hand, increasing the amount of titanium in solution restrained precipitation of niobium; this was particularly the case when the amount of niobium pentoxide was less than 1-2 mg. In order to speed up coagulation, the solution was heated for 2-3 hours. The precipitate which separated out was reprecipitated. The precipitates of niobium pentoxide were tested after a two fold precipitation for their content of titanium by the colorimetric method with hydrogen peroxide. It was found that the content of titanium dioxide in the niobium pentoxide precipitates varied within the limits 0.0-0.2 mg.

Results for determination of niobium pentoxide are given in Tables 1-3.

TABLE 1

Determination of Niobium Pentoxide in a Standard Solution in the Presence of Ascorbic Acid.

Amount taken in g		Ratio $Nb_2O_3 : TiO_2$	Amount of Nb_2O_3 found in g	Error in g	TiO_2 found in Nb_2O_5 in g
Nb_2O_5	TiO_2				
0.0036	0.0914	1 : 25	0.0035	−0.0001	0.0000
0.0036	0.0914	1 . 25	0.0039	+0.0003	0 0001
0.0036	0.0914	1 : 25	0.0038	+0.0002	0.0002
0.0036	0.0914	1 : 25	0.0039	+0.0003	Traces
0.0036	0.1524	1 : 42	0.0037	+0.0001	0.0001
0.0036	0.1524	1 : 42	0.0038	+0.0002	0.0000
0.0036	0.1524	1 : 42	0 0037	+0.0001	0.0000

On the basis of the results of our experiments the following method can be recommended for determining niobium in the presence of large amounts of titanium.

0.5 g of finely ground titanium slag (perovskite) is placed in a platinum dish and wetted with water; 2-3 ml of sulfuric acid (1:1) is then added followed by 4-5 ml of hydrofluoric acid, and the contents of the basin carefully mixed with a platinum spatula. When organic matter is present, it is recommended that the basin plus test material be heated for 20-30 minutes in a muffle at 600-700°. In order to decompose the test material, the basin is placed on a sand bath and heated, first gently, and then, after removing most of the hydrofluoric acid, more strongly until the appearance of white fumes; these white fumes are allowed to continue for 10-15 minutes. Basin and contents are cooled and 2-3 ml of water added; the whole is mixed and then evaporated on a sand bath until the residue obtained is almost dry. After cooling, 5 ml of water is added, followed by 10 ml of hydrochloric acid sp. gr. 1.19.; the mixture is heated on a sand bath for 5-10 minutes, and then transferred to a 300 ml beaker, the basin being rinsed with cold water. 0.1 g of ascorbic acid and 2 g of ammonium chloride are added to the solution, which is then diluted with water to 180 ml and heated to 50°; niobium is precipitated with 10-20 ml of a freshly prepared 1% aqueous solution of tannin. Tannin is added dropwise while the solution is continuously stirred. After some time, when the solution has become turbid, a small amount of macerated paper is added, and for complete removal of niobium tannate, solution plus precipitate are heated for 2-3 hours at 50°. After cooling, the precipitate is filtered through a 7-9 cm diameter filter paper (white ribbon grade), and washed 6-8 times with a cold 4% solution of hydrochloric acid, the precipitate being transferred quantitatively during this operation onto the filter paper. Filter paper plus precipitate are placed in a tared platinum crucible and carefully ignited and ashed, after which the crucible is heated with a Meeker burner or in a muffle at 1000°. The crucible is cooled for 20 minutes in a desiccator and weighed. If the precipitate is pure white in color it is fused with 0.5 -1.0 g of potassium pyrosulfate and the fused melt dissolved in 20 ml of 5% sulfuric acid, to which 1-2 drops of hydrogen peroxide is then added. A pale yellow color of the solution indicates the presence of titanium. In this case the solution is transferred to a 25 ml standard flask; it is then mixed and the color compared with the color of a standard solution of titanium. The amount of titanium dioxide found is calculated from the weight of the precipitate of niobium pentoxide. In the presence of titanium the calcined precipitate of niobium pentoxide sometimes has a grey color in addition to the white color. In such cases it is necessary to carry out a second precipitation. In order to do this, the calcined precipitate is moistened with 2-3 drops of water, and 8-10 drops of sulfuric acid (1:1) added (when the weight of niobium pentoxide precipitate is 15-20 mg, 20 drops of sulfuric acid are added), followed by 1-2 ml of hydrofluoric acid, and the crucible is put on a sand bath; it is then heated genly at first until the precipitate is completely dissolved, and finally it is heated more strongly until white fumes are evolved. After white fumes

TABLE 2

Determination of Niobium Pentoxide in Titano-Magnetite

Weight of titano-magnetite taken (14% TiO_2), in g	Nb_2O_5 added		Ratio of Nb_2O_5 : TiO_2	Nb_2O_5 found		Error		TiO_2 found in Nb_2O_5, in g
	In g	In %		In g	In %	In g	In %	
0.5	0.0183	3.66	1 : 4	0.0185	3.70	+0.0002	+0.04	0.0002
0.5	0.0183	3.66	1 : 4	0.0184	3.68	+0.0001	+0.02	0.0002
1.0	0.0036	0.36	1 : 39	0.0037	0.37	+0.0001	+0.01	Traces
1.0	0.0018	0.18	1 : 78	0.0017	0.17	−0.0001	−0.01	0.0001
2.0	0.0036	0.18	1 : 78	0.0034	0.17	−0.0002	−0.01	0.0001
2.0	0.0018	0.09	1 : 155	0.0017	0.09	−0.0001	0.00	

have been coming off for five minutes the crucible is cooled and a few drops of water added , evaporation is repeated and this time carried on until only one or two drops of sulfuric acid remain in the crucible. After cooling 1-2 ml of water is added to the crucible, followed by 5 ml of hydrochloric acid sp.gr. 1.19, and the solution transferred to a 100 ml beaker; the crucible is rinsed a few times with cold water, the solution being made up to 80-90 ml during this operation. 0.05 g of ascorbic acid is added to the solution and niobium precipitated in the cold with 10-20 ml of a freshly prepared 1% aqueous solution of tannin; the latter is added dropwise with continuous stirring.

TABLE 3

Determination of Niobium Pentoxide in Perovskites and Titanium Slags

Sample	gm. of sample taken	Nb_2O_5, in %
Perovskite	0.5	0.87; 0.88; 0.91
	0.5	0.89: 0.92; 0.92
	0.5	0.88; 0.87; 0.87
	0.5	0.74: 0.73; 0.73
	0.5	0.90: 0.91; 0.92
Titanium slag	0.5	0.42; 0.39
	0.5	0.39; 0.39; 0.33
	0.5	0.27; 0.23
	0.5	0.32; 0.35
	0.5	0.30; 0.29; 0.29

Since, during the second precipitation a small amount of titanium might be found in solution, the niobium precipitate is removed very rapidly. A small amount of macerated paper is added to the solution which is then left overnight. The precipitate is filtered through a 7 cm diameter filter paper (white ribbon grade) and washed 5-6 times with cold 4% hydrochloric acid. Filter paper plus precipitate are placed in a small tared platinum crucible and are ashed; the residue is tested for its titanium content, the latter being determined colorimetrically using the hydrogen peroxide method; if titanium should be found to be present the weight of titanium dioxide found should be subtracted from the weight of niobium pentoxide.

SUMMARY

A rapid and accurate method has been developed for determining niobium in the presence of large amounts of titanium; it is based on precipitation of niobium with tannin in 5% hydrochloric acid solution in the presence of ascorbic acid which forms a complex with titanium.

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CHROMATOGRAPHIC SEPARATION OF LITHIUM AND MAGNESIUM

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A number of papers have been published which have been devoted to separating magnesium from the alkali metals. Thus sodium, potassium, rubidium, and magnesium [1] have been separated on Dowex-50 and Amberlite IR-100 with 0.2 N hydrochloric acid. Sodium was separated quantitatively, but the elution curves for the other elements partially crossed each other. Sodium, potassium, and magnesium [2] have been separated on Dowex-50 with 0.7 N hydrochloric acid, while sodium, potassium, rubidium, and cesium [3] were separated with 0.15 N hydrochloric acid. In the first case, separation was complete, while in the second case sodium and potassium were completely separated, but separation of rubidium and cesium was incomplete. A method has been published for the separation of lithium and magnesium [4]. In this method the mixture of solutions of lithium and magnesium is adjusted to pH 13 by addition of sodium hydroxide; magnesium is thereby precipitated. Magnesium hydroxide is filtered off while the filtrate containing the lithium is concentrated on a column packed with aluminum oxide. Separation of such a system by the method of precipitation chromatography is difficult, since lithium and magnesium which possess similar chemical properties, give equally sparingly soluble precipitates. The exception is their hydroxides, which have different solubilities. The solubility of $Mg(OH)_2$ is 9×10^{-3} g, while that of LiOH is 12.8 g per 100 g of water. Consideration of published results gives one reasons for assuming that, by analogy with separation of magnesium and the alkali metals, it should be possible to separate lithium and magnesium by simple displacement with hydrochloric acid.

Analysis of elution curves obtained on various sorbents enabled us to choose the most suitable sorbent for separating lithium and magnesium. Elution curves were obtained for the resins SBS, SBSR, SDV-3, and KU-2. These curves were obtained by passing an equinormal mixture (0.07 N) of lithium and magnesium through a column 25 cm long of resin until eluates whose concentration is the same as that of the original solution appear.

The eluate was analyzed for its lithium and magnesium content after separation of these metals. The hydroxyquinoline method was used for separating lithium and magnesium, the magnesium being determined photometrically [5]. After removal of magnesium, the lithium was determined flame photometrically and by the the reaction with potassium ferriperiodate [6, 7]. Magnesium was detected qualitatively in the alkali solution by means of diphenylcarbazide or quinalizarin.

When resins SBS and SBSR were used, both elements appeared in the first fraction of eluate. On passing the mixture through resin SDV-3, the lithium appeared in the second fraction of eluate, and magnesium in the eighth. When resin KU-2 was used, lithium appeared in the third fraction and magnesium in the eleventh (each fraction was 25 ml).

Thus, for the system under consideration, the resins can be order of resolving power as follows: SBS = SBSR < SDV-3 < KU-2.

In order to carry out the tests under the strictest conditions, resolution was carried out on resin SBS in the H-form in a column 1.2 cm in diameter and with a resin length of 25 cm. 40 ml of an equinormal (0.07 N) solution of lithium and magnesium was passed through the column. After adsorption the column was washed with water. The column was then washed with 0.25 N hydrochloric acid at the rate of 1 ml/cm^2/min.

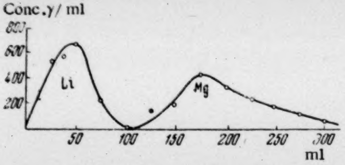

Fig. 1. Elution curves for lithium and magnesium during elution with 0.25 N HCl

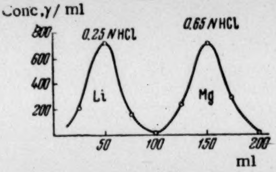

Fig. 2. Elution curves during elution of lithium with 0.25 N HCl and of magnesium with 0.65 N HCl

Two peaks corresponding to lithium and magnesium respectively were obtained on the elution curves (Figs. 1-3). The magnesium peak was not drawn out so much, and resolution was more complete on using 0.65 N hydrochloric acid for elution. This displacement method is fairly simple and effective; all the adsorbent is not used however, but only a small part of its upper layer. Accordingly instead of using this technique, based on displacement with acid for separating lithium and magnesium, it is sometimes profitable to separate these two cations by means of alkali from a column saturated all along its length, by making use of differences in solubility of the hydroxides of these metals. The following technique was used for the latter method: a resin column 20 long and 1 cm in diameter was saturated with an equinormal (0.05 N) mixture of lithium and magnesium ions (500 ml); the column was then washed with water and eluted with 0.15 N NaOH. Only lithium could be detected in the eluate. Magnesium was eluted with 0.65 N hydrochloric acid. The technique described allows one to get solutions containing on the one hand lithium and magnesium, and on the other, a mixture of sodium and magnesium. In those cases where the presence of sodium in mixtures with lithium or magnesium respectively is preferable to the original combination of lithium and magnesium, such a method of resolution is completely justified.

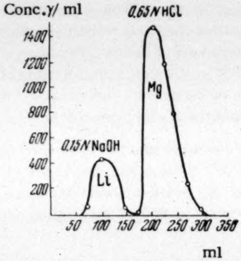

Fig. 3. Elution curves for elution of lithium with 0.15 N NaOH and of magnesium with 0.65 N HCl

SUMMARY

1. It has been demonstrated that lithium and magnesium can be separated by simple displacement with 0.25 and 0.65 N hydrochloric acid from an ion-exchange column.

2. In order of resolving power for lithium-magnesium mixtures Russian produced ion-exchange resins can be arranged in the following series: SBS = SBSR < SDV-3 < KU-2.

3. Lithium and magnesium can be separated by eluting the column successively with 0.15 N alkali and 0.65 N hydrochloric acid, the latter being used for removing magnesium.

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DETERMINATION OF BORON IN ROCKS BY NEUTRON ANALYSIS

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The absorption cross-section or capture of neutrons by the nucleus of the boron atom is three or four times greater than the neutron capture of the major rock forming elements (Table 1). Capture of neutrons by the boron nucleus is not accompanied by emission, as is usual, of hard gamma quanta; during the nuclear reaction B^{10} (nα) Li^7 however, the nucleus splits up with emission of heavy charged particles.

TABLE 1

Effective Thermal Neutron (E= 0.025 ev) Capture and Scatter Cross Sections of the Nuclei of the Major Rock-Forming Elements.

Element	H	B	C	N	O	Na	Mg	Al	Si	S	K	Ca	Fe
Capture cross section σ_s (barns)	0.329	752	0.0042	1.78	0.0002	0.5	0.059	0.215	0.13	0.49	0.97	0.43	2.43
Scatter cross section σ_s (barns)	gas 38	4	4.8	10	4.2	4.0	3.6	1.4	1.7	1.1	1 5	9	11

Thanks to these characteristics, boron is widely used in nuclear physics as an effective indicator and absorber for neutrons [1 - 3]. The method of neutron radiography has been used for the study of distribution in fine microsections of inclusions which weaken neutron beams [4].

During bombardment of boron containing sample by neutrons there is observed a weakening in the density of the neutron beam, the extent of the weakening being dependent on boron content. This fact enables one to determine boron quantitatively without any preliminary treatment of test sample. The possibility of carrying out such a determination of boron was first demonstrated experimentally by Martelly and Sue in 1946 [5]. Developments in experimental technique in the field of nuclear physics have enabled us to develop a method for determining the boron content of rocks.

A. Apparatus and Measurement Technique

The principle parts of the setup are a "neutron beam" using water as a retarder, and measuring apparatus (Fig. 1). The neutron source was a preparation of Po + Be with a power of 2-4 Curies.

A test sample in a copper box 50 cm^3 capacity and with an internal tight fitting lid was placed between the detector and the directed neutron beam. The detector was a scintillator with added boron. The use of boron as filler in the scintillator is based on the fact that the ionizable particles which originate during capture of neutrons when nuclear fission occurs leads to light flashes in the phosphor which are registered by the photomultiplier.

Satisfactory results were obtained by using a scintillator (see below) with a ratio of ZnS/ B = 3.5.

Amorphous boron (with a brown color) was used for adding to the zinc sulfide; although scintillators prepared in this way are dark, all the same their efficiency is higher than when boron is added in the form of its light colored compounds. The efficiency of the scintillators was not determined, but in practice it proved sufficient for carrying out measurements under the geometrical conditions used for the setup (Fig. 1). When the power n- of the source was 2 Curies, counts of the order of 2000 impulses per minute were ensured for samples not containing boron.

Light signals were amplified by a photomultiplier built along conventional lines; the impulses were then fed to a counting apparatus.

Test samples were measured for 10 minutes. The stability of operation of the photomultiplier was controlled every 1-2 measurements by reference to a control sample which was free from boron. It is convenient to keep such control samples, which are characteristic of the type of rock being examined, in separate boxes, in order to avoid frequent overfilling. The boron content of test samples was determined by means of a standard curve which had been constructed on the basis of samples with a known amount of boron; in this curve the value of the ratio $(N/N_{c,s.})100\%$ in percentages was plotted along the ordinate, where N and $N_{c.s.}$ are the cross-sections for test and control samples respectively.

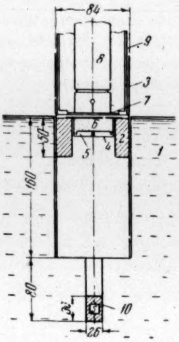

Fig. 1. Schematic diagram of the setup:
1) water (56 liters); 2) paraffin ring; 3) directing tube; 4) box; 5) box with tight fitting lid; 6) test sample; 7) scintillator; 8) photomuliplier; 9) photomuliplier case; 10) neutron source S in a paraffin capsule.

On Fig. 2. is shown a calibration curve for a sample of weight 50 g containing up to 30% B_2O_3. At B_2O_3 contents greater than 3% the curve flattens out so that determination becomes difficult.

During a study of the possibility of using that part of the curve which has a steep slope for determining any amount of boron, it was established that for test types of rocks (calcifer and magnetite ores) the slope of the curve is determined only by the surface density of boron; accordingly, for analysis of ores with high boron contents, it is necessary to cut down the amount of sample taken. This is illustrated on Fig. 3, where curve 1 was constructed for 50 g samples and curve 2 for 25 g of magnetite. On changing the horizontal scale by a factor of two, so that results of measurements are related to the same surface density of boron, then the curves for samples weighing 25 and 50 g coincide satisfactorily. It would appear best to use the steep part of the curve for determining very large amounts of boron (up to 15 and 30% B_2O_3) in conjunction with sample weights of 10 and 5 g. Practice showed that for small sample weights, relation between the nature of the curve and surface density of boron is the same, with decreasing sample weight; however, the accuracy of a single determination decreases. This is explained by the fact that when very small samples are used, it is difficult to keep the relative thickness of the layer of test material constant. It is necessary to keep this thickness constant, since the light sensitivity of the photomultiplier cathode and the efficiency of the phosphor are not uniform with area. Under such conditions, therefore, it is necessary to carry out 6-8 measurements for various positions of the photomultiplier in order to get reliable results. For this reason, when there is sufficient amount of ground up ore, it is less difficult and more reliable to dilute test samples with a high boron content with ore which is free from boron, and to carry out determinations with aliquots of 50-25 g of this diluted material.

B. Effect of the Elemental Composition of Test Material on Accuracy of Measurement

In Table 2 are given calculated results for neutron absorption by various rocks. For greater clarity the neutron absorption of a rock is expressed in units which are equivalent to boron content. Calculations were made on the basis of the formula

$$C_B = \frac{C_{el}\,\sigma_{el.}\,A_B}{\sigma_B\,A_{el}},$$

where C_B and $C_{el.}$ are the percentage contents of boron and element in the test; A_B and $A_{el.}$ are the atomic weights of boron and element; and σ_B and $\sigma_{el.}$ are the cross-section of capture of thermal neutrons by boron and the element.

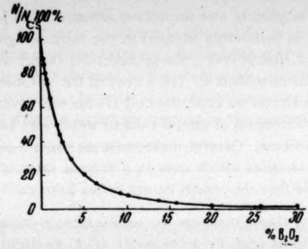

Fig. 2. Relation between absorption of thermal neutrons and boron content in samples weighing 50 g.

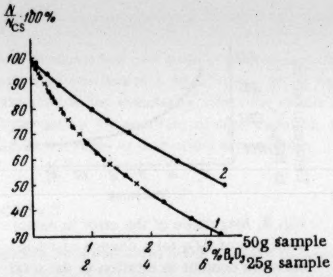

Fig. 3. Relation between absorption of thermal neutrons and boron content of sample:

1) for 50 g samples of calcifer and magnetite; 2) for 25 g samples of magnetite. The points on curve 2 which are related to sample weight of 50 g by changing the horizontal scale are denoted by crosses.

TABLE 2

Absorption of Neutrons by Various Rocks

Sample number	Type of rock	Average chemical composition	Absorption in units equivalent to boron content (calculated)	Experimental results in units equivalent to boron content
1	Dry sand	SiO_2	0.00317	0
2	Moist sand	SiO_2 85; H_2O 15%	0.01072	0.22
3	Water	H_2O	0.0534	0.63
4	Magnetite	Fe_3O_4	0.0459	0.05
5	Serpentite	MgO 43%; SiO_2 44%; H_2O 13%	0.00928	0.17÷0.20
6	Calcifer (dolomite)	CaO 30.4%: Mg 21.7%: CO_2 47.9%	0.00396	~ 0.01

Taking the sensitivity of the method as 0.2% of B, we see that absorption by rocks 1, 2, 5, and 6 is either lower than, or within the limits of accuracy of the measurement. The last column contains results obtained during measurement of these same rocks relative to dry sand and in the same units which are equivalent to boron content. On comparing calculated results with experimental results, it can be seen that for those samples where appreciable amounts of hydrogen are not present, the order of the value of weakening of neutrons by the rock agrees with the calculated value. For samples which contain hydrogen, weakening of the neutrom beam by the rock, as a result of scattering, is 10-20 times greater than the calculated value when only absorption is taken into account. These results show that: 1) a change in chemical composition of test samples does not lead to serious errors in boron determination; 2) the main source of error in this connection is hydrogen when it is present, since the large scattering effect which it introduces may lead to serious errors when the hydrogen content of test sample varies. On Fig. 4 is shown the error in determining boron (in terms of B_2O_3) when the moisture content varies by 1%. The value of this error decreases with increasing water content.

For this reason, analysis of rocks of different types must be based on calibration curves which have been drawn up on the basis of control samples whose water content is the same as that of the test samples.

C. Effect of Volume of Sample on the Final Result

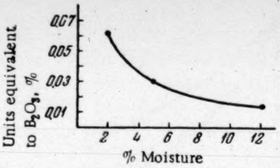

Fig. 4. Magnitude of the error in determination of B_2O_3 for a change of 1% in moisture content in relation to the total water content of 50 g of test sample.

Some rocks which are similar in chemical composition differ appreciably with respect to their density (e.g. serpentite and serpentine asbestos rocks); accordingly in comparing samples of the same weight but from different rocks, the geometrical factor would appear to be affected. The effect of the volume of test test material on experimental results was investigated on two samples of quartz sand to which was added powdered silica. Careful measurements carried out on these samples which were in a volume ratio of 0.7:1, showed that the results do not differ from each other.

Table 3 contains the results of analyzing boron containing ores, by a chemical (G.E. Kurilchikov) method, and by the neutron method respectively. The satisfactory agreement between the results of analysis by these two methods (± 20%) shows that boron can be determined fairly accurately by the neutron analysis method.

The method can be use for determination of manganese and rare earths in ores, but its possibilities are considerably restricted. Thus, a change in manganase content (σ_3 = 12 barns) of 30% leads to weakening of a neutron beam by only 18%. The limit of the sensitivity of the method for determination of dysprosium (σ_3 = 1100 barns) amounts to 0.08%, while for gadolinium (σ_3 = 4400 barns) it is about 0.002%.

D. Preparation of Boron-Containing Scintillators

TABLE 3
Comparison of Analytical Results for Ores by Chemical and Neutron Methods

Sample number	Boron found in a magnetite-ludwigite medium, in %	
	By a chemical method	By neutron analysis
1	2.10	2.40
2	2.76	2.92
3	1.94	2.17
4	2.54	2.20
5	2.00	1.80

The following solution and reagents are necessary for preparing boron-containing scintillators:

1) a 1.6% solution of strontium nitrate.

2) a 20% solution of potassium silicate (80.5 g of anhydrous KOH and 119 g of SiO_2 are dissolved in 1 liter of water with heating and continous agitation.

3) Amorphous boron, ground in an agate mortar and sieved through a silk sieve.

4) Luminophor (K-5 grade was used).

5) The mixture of luminophor and boron was prepared by simple mixing of the components in the ratio luminophor/ boron = 3.5.

6) A standard solution of potassium silicate plus coagulator (15-20 ml of 1.6% strontium nitrate solution was diluted to 1 liter with distilled water; to the solution thus obtained was added, slowly and with thorough mixing, 60 ml of 20% potassium silicate solution).

On the bottom of a 2 liter crystallizing basin were placed degreased glass discs (8 of them) and standard solution (about 900 ml) poured over them. 50-100 ml of the same standard solution was transferred to a a separating funnel, to which was then added the mixture of luminophor and boron in an amount sufficient to give 10 mg of mixture per cm^2 of the bottom of the crystallizing basin. The suspension thus obtained was then poured from the funnel, after mixing, into the crystallizing basin through a funnel sprayer. The suspension was left for 1.5 hours, after which it was carefully siphoned off. The scintillators were dried with hot air.

In conclusion we should like to thank A.P. Vinogradov for his continuous interest in the work, and to express our indebtedness to V.I. Baranova for valuable advice in carrying out the present work, and to K.D. Tolstoy and V.L. Barsukov for consultation.

SUMMARY

A technique has been developed for determining boron in minerals and ores without preliminary chemical treatment of test samples; the accuracy of a single determination amounts to ± 3% relative. It has been established that changes in the elemental composition of test samples do not essentially affect the results obtained for boron. In order to avoid the negative influence of hydrogen on the accuracy of determination, it is essential that the hydrogen content of the control sample should be the same as that of the test sample.

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DETERMINATION OF UNIVALENT THALLIUM BY RADIOMETRIC TITRATION WITH SODIUM TETRAPHENYLBORON

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A number of methods are known for the determination of thallium [1]. The present article consists of a description of a radiometric titration of univalent thallium with sodium tetraphenylboron *. This reagent has found wide application for gravimetric and titrimetric determinations of potassium [2, 3]. There are also published results on the determination of Ag, Rb, Cs, and NH_4 [4, 5] by means of sodium tetraphenylboron. The composition of the precipitates formed by these ions correspond to the formula $MeB(C_6H_5)_4$. The solubilities of $KB(C_6H_5)_4$, $RbB(C_6H_5)_4$, $CsB(C_6H_5)_4$ are 1.5×10^{-4}, 4.5×10^{-5}, 2.9×10^{-5} moles/liter, respectively.

Apparatus and Titration Technique

An apparatus which has been described in the literature [6] for measurement of actitivity was modified somewhat. In Fig. 1 is shown the apparatus used for radiometric titration; it consists of a torsion counter, a glass reservoir with capillary tubes (Fig. 3) placed in lead housing, micro-filtering tubes (Fig. 2), and an electric impulse counter.

Test solution was sucked up by a syringe and transferred to the reservoir where its activity was measured; the solution was then returned to a beaker and the next lot of reagent added to it. Using the results of actitivity measurements, and taking into account changes in volume of the solution, a titration curve was constructed. The equivalence point was thus determined graphically.

Determination of Thallium in Solutions

The stock solution of $TlNO_3$ was prepared by dissolving an aliquot of metallic thallium in concentrated nitric acid. The concentration of the sodium tetraphenylboron solution was established gravimetrically by means of potassium chloride [7].

Univalent thallium forms a white fine crystalline precipitate with $NaB(C_6H_5)_4$. The sensitivity of the reaction is 9γ/ml.

Experiments showed that 1 mole of $NaB(C_6H_5)_4$ is required to precipitate 1 mole of thallium nitrate. Consequently, the composition of the compound formed corresponds to the formula $TlB(C_6H_5)_4$.

We established by means of the radiometric method [8] that the solubility of $TlB(C_6H_5)_4$ is 6×10^{-7} mole/liter (the solubility of TlI is 2.4×10^{-4} mole/liter). Precipitation of thallium as $TlB(C_6H_5)_4$ is therefore completely suitable for quantitative analysis.

The radioactive indicator used was Tl^{204} with a specific actitivity of 150 mC/g. 0.05 ml of indicator was added to the test solution so that the initial activity in each case was not greater than 2000 impulses/minute. The volume of solution transferred to the reservoir was 2-2.5 ml.

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* The reagent was synthesized in the Organic Chemistry Department of Moscow University and was kindly given to us by V. A. Sazonova, to whom the authors are very grateful.

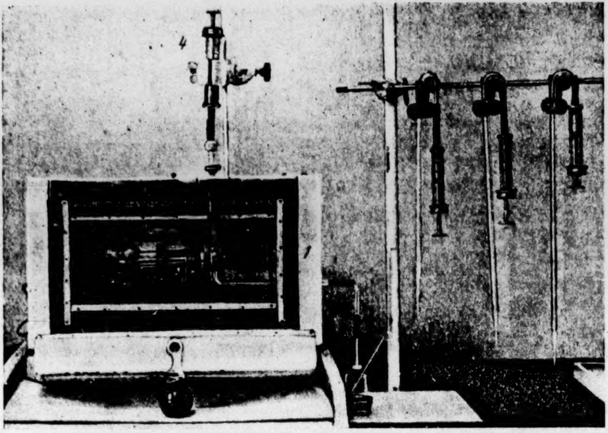

Fig. 1. Apparatus for radiometric titration:
1) Lead housing; 2) glass reservoir; 3) torsion counter; 4) syringe for sucking up solution; 5) micro-filtering tube.

Titration was carried out at pH 5, since on increasing the acidity, the decomposition product $HB(C_6H_5)_4$ [7] appears in solution. A few crystals of CH_3COONa were added to the test solution in order to get the necessary pH value. The solution of $NaB(C_6H_5)_4$ was stable for a week after preparation. On standing for a longer time, the solution became turbid and acquired a darker color. It is probable that this was the result of organic impurites present in the preparation of $NaB(C_6H_5)_4$, since the normality of the solution remained practically unchanged for three weeks.

In Fig. 4 is shown the curve obtained by titrating 0.93 mg Tl with about 0.02 M $NaB(C_6H_5)_4$, while Table 1 contains the results obtained during titration of various amounts of thallium. Titration of one sample takes 20-30 minutes. This time can be shortened by basing determination on only two points [9].

Thallium was also determined in the presence of Cd, Zn, Pb, Cu, In, and Fe. Some divalent elements decompose the reagent. Thus the reaction with divalent mercury proceeds as follows [10]:

$$LiB(C_6H_5)_4 + 4HgCl_2 + 3H_2O = 4C_6H_5 \cdot HgCl + LiCl + 3HCl + H_3BO_3.$$

Cu, Ce, La, and Th also form precipitates with a solution of sodium tetraphenylboron; these precipitates appear to be the hydroxides of these elements, or may be diphenyl, which is formed during decomposition of the reagent. The reaction proceeds as follows:

$$2LiB(C_6H_5)_4 + MeCl_2 + 6H_2O = Me(OH)_2 + 2LiCl + 2C_6H_5 \cdot B(OH)_2 + 6C_6H_6;$$

with cupric ions, diphenyl is formed during the reaction:

$$2LiB(C_6H_5)_4 + 2CuCl_2 = 2CuCl + 2LiCl + 2B(C_6H_5)_3 + C_6H_5 \cdot C_6H_5.$$

A saturated aqueous solution of Complexone III (Trilon B) was added to the test solution in order to eliminate interference from some of these elements during determination of thallium in their presence.

Table 2 contains the results obtained during titration of thallium in the presence of other elements. Complexone III was added during determination of thallium in the presence of copper and lead. These elements, in amounts which are almost one hundred times that of thallium, did not interfere.

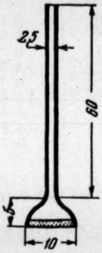

Fig. 2. Micro-filtering tube.

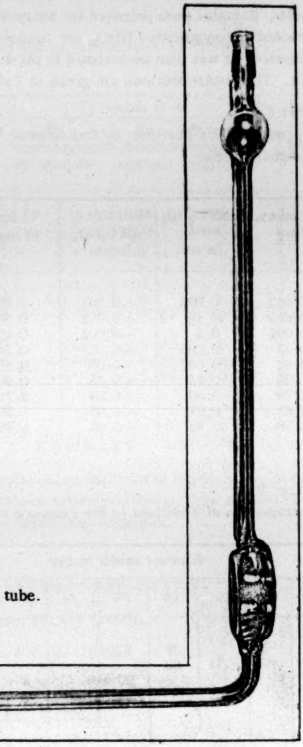

Fig. 3. Glass reservoir for measuring the activity of the solutions.

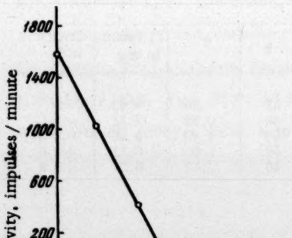

Fig. 4. Radiometric titration curve for 0.93 mg of thallium (in 2 ml) with a solution of NaB–(C$_6$H$_5$)$_4$

The amount of thallium was also calculated on the basis of two points using the following formula:

$$Ve = \frac{V_2(A_1 - B) - V_1(A_2 - B)}{A_1 - A_2}$$

where V_1 and V_2 are the volumes of titrant; A_1 and A_2 are the activity of the test solution after addition of V_1 and V_2; B is the background; and V_e the equivalent volume of titrant.

Table 3 contains results for determination of thallium by this method.

We applied this method of determining thallium by radiometric titration with sodium tetraphenylboron for analyzing a number of production samples, and obtained satisfactory results. Samples were prepared for analysis as follows: an aliquot of 0.1 - 0.3 g was dissolved in the minimum amount of concentrated HNO_3, the insoluble portion was filtered off, and the remaining solution partly evaporated; it was then neutralized to pH 4-5 and titrated (where necessary, in the presence of Complexone III). The results obtained are given in Table 4. *

TABLE 1

Determination of Thallium by Radiometric Titration with Sodium Tetraphenylboron

Tl taken, in mg	$NaB(C_6H_5)_4$ used, in ml.	Molarity of $NaB(C_6H_5)_4$ solution	Tl found, in mg	Error in %
0.022	0.066	~0.002	0.020	—9.1
0.045	0.16	~0.002	0.048	+6.6
0.091	0.3	~0.002	0.091	0
0.23	0.036	~0.03	0.24	+4.3
0.46	0.067	~0.03	0.46	0
0.93	0.14	~0.03	0.95	+2.1
2.79	0.40	~0.03	2.72	—2.5
4.65	0.67	~0.03	4.56	—1.9
5.58	0.82	~0.03	5.58	0

Table 2

Determination of Thallium in the Presence of Other Elements

Amount taken in mg							Tl found in mg	Error in %
Tl	Cd	Zn	Cu	Pb	In	Fe		
0.93	36		39	62			0.93	0
0.93	109	34	80				0.93	0
0.93				37		30	0.90	—3.3
0.93						70	0.90	—3.3
0.93					60		0.95	+2.1
0.93		120					0.96	+3.3

TABLE 3

Determination of Thallium on the Basis of Two Points

Tl found, in %	V_1	A_1	V_2	A_2	B	V	Tl found, in mg	Error in %
0.93	0.1	945	0.2	508	52	0.30	0.93	0
2.79	0.2	986	0.45	644	46	0.88	2.72	—2.5
4.65	0.7	934	0.9	702	50	1.46	4.53	—2.5
5.58	0.4	1354	0.7	1086	50	1.65	5.73	+2.6
6.51	0.6	1180	1	882	46	2.12	6.57	+0.9

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* Simultaneously with our work, Wendlandt published an article [11] in which he suggested gravimetric determination of thallium by the same reagent.

TABLE 4

Determination of Thallium in Ores and in Intermediate Products

Main components of sample	Weight taken, in g	Tl found, in %			Method used for establishing the equivalence point
		By spectrographic analysis	By chemical analysis	By radiometric titration	
Cd	0.1139	>0.1	>0.12	0.11	Graphically
Cd	0.1446	>0.1	>0.12	0.14	»
Pb, Cd, Cu, Zn	0.1035	0.1	0.14	0.14	»
Pb, Cd, Cu, Zn	0.1039	0.1	0.14	0.17	»
Cu	0.1050	~0.1	0.1	0.14	»
Cu	0.1023	~0.1	0.1	0.14	»
Pb, Cu, Zn, Cd	0.1678	~0.01	0.017	0.016	On the basis of two points
Pb, Cu, Zn, Cd	0.2099	~0.01	0.017	0.018	»
Cd, Pb, Zn, Sb, Fe	0.3266	~0.01	0.009	0.007	»
Cd, Pb, Zn, Sb, Fe	0.3533	~0.01	0.009	0.007	»

SUMMARY

A method has been developed for determining thallium (in the presence of Cu, Cd, Zn, Pb, In, and Fe) by radiometric titration with a solution of sodium tetraphenylboron. The method of radiometric titration is applicable to the analysis of technical samples containing thallium.

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A SPECTROGRAPHIC METHOD OF DETERMINING SCANDIUM IN MINERALS, ORES, AND PROCESS PRODUCTS

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Scandium is one of the most widely distributed rare earth elements which usually occur in a very diffused state. The number of scandium minerals is small, and only three minerals are known which contain large amounts of scandium these are: thortveitite - (Sc, Y) Si_2O_7, wickite, and bazzite. Vernadsky [1]; has pointed out that scandium is often met in pegmatite minerals. Goldschmidt [2] found larger amounts of scandium (0.1 - 1% Sc_2O_3) in wolframites from Tsinnwald. During studies of minerals of the Soviet Union, Borovik [3] found a high content of scandium in khlopinite (more than 0.5% scandium) and beryl.

Chemical methods for determining scandium, in view of their complexity, have not found wide application; our information on detection of scandium is based to a considerable extent on results obtained by the spectrographic method. Determination of scandium in various materials by spectrographic methods has been carried out by Goldschmidt [2], Van Tongeren [4], Kvalheim and Strock [5], Oftedal [6], Ahrens [7], and Borovik [8].

Our work consists of two parts: one is devoted to direct quantitative spectrographic determination of scandium in khlopinite, wolframite, cassiterite, and beryl, while the other is devoted to a universal spectrochemical method of determining scandium in minerals and ores of different composition.

Determination of Scandium in Khlopinite, Wolframite, Cassiterite, and Beryl

For the determination of scandium in khlopinite [(Y, U, Th) Nb, Ti, Fe]$_2$O$_6$ wolframite [Mn, Fe (WO_4)], cassiterite, SnO_2, and beryl [$Be_3Al_2(Si_{16}O_{18})$] a D.C. arc between graphite electrodes was used as excitation source.

Test material was fed into the arc flame by evaporation from an opening in the graphite electrode (anode) of a mixture of the mineral with graphite powder containing lanthanum oxide as reference element.

Taking into account the fact that scandium is one of the difficultly volatile elements, evaporation was carried out from thin walled sharpened electrodes. The shape of the electrodes is shown in Fig. 1.

The spectra were photographed on a quartz autocollimating spectrograph with high dispersion (KSA-1), fitted with a one lens condenser; they were photographed as follows: an aliquot of the mineral (20 mg) was mixed with carbon powder (10 mg) containing 2.5% lanthanum oxide, and the mixture loaded into the cavity in the graphite electrode; the diameter of the cavity was 2 mm while the depth was 7 mm. A D.C. arc was struck between the vertically fixed electrodes. During the first 30 seconds of arc burning, the current was 5 amperes; it was afterwards increased to 10 amperes. The duration of arc burning was established on the basis of curves characterizing the rate at which scandium evaporates from the various minerals, and was taken as 2.5 minutes for khlopinite, wolframite, and beryl, and 3 minutes for cassiterite (Figs. 2, 3, and 4).

The arc gap was 3 mm and was kept constant during burning of the arc. A sharp image –magnified threefold– of the central part of the arc flame was projected on the spectrograph slit. The photographic material used was reproducing plates with a sensitivity of 5 GOST units, or "Spectrographic" type II with a sensitivity of 8 GOST units.

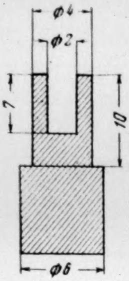

Fig. 1. Form of the electrode (dimensions in mm).

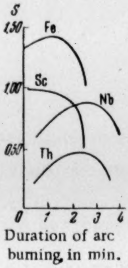

Fig. 2. Change in blackening of the lines of Sc, Th, Nb, and Fe during evaporation of khlopinite.

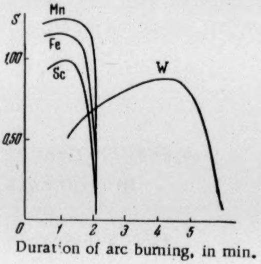

Fig. 3. Change in blackening of the lines of Sc, Fe, Mn, and W during evaporation of wolframite.

During selection of the reference element, members of the rare earth group were tested since they behave similarily to scandium [9]. We used lanthanum, which, for the most part is not present in the test samples we examined, and burns in the arc at the same time as scandium. As an example, we have shown in Fig. 5 the changes in blackening of the lines of scandium and lanthanum during evaporation of wolframite containing both these elements. It should be noted that the use of lanthanum as a reference element increases the accuracy of scandium determination approximately twice as compared with results obtained during determination of scandium on the basis of the absolute blackening of its lines.

Determination of scandium concentration was carried out on the basis of calibration curves constructed within the parameters: logarithm of scandium concentration - difference in blackening of scandium and lanthanum lines. The following pairs of lines were used:

Sc II 2552.36	La II 2610.34
Sc II 3253.7	La II 3376.33

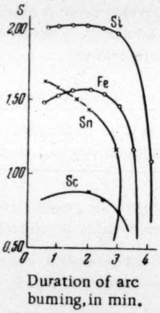

Fig. 4. Change in blackening of the lines of Sc, Sn, Fe, and Si during evaporation of cassiterite.

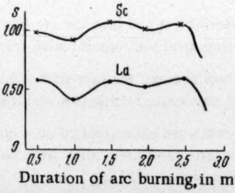

Fig. 5. Change in blackening of scandium and lanthanum lines during evaporation of wolframite containing these elements.

Scandium was determined within the concentration range 0.01 to 0.5% with a probable error for a single determination of ± 6- 12%. During direct determination of scandium in the minerals listed above, a special series of standards was prepared for each mineral. Minerals in whose arc spectra scandium was absent were used for preparing the standards; scandium was added as scandium oxide.

One of the drawbacks of the direct method of determining scandium is the necessity of preparing separate standards for each mineral. The use of any one series of standards, as Fig. 6 shows, is not possible, since differences in the composition of test minerals lead to a shift of the calibration curves.

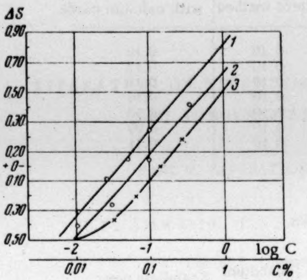

Fig. 6. Calibration curves for khlopinite, wolframite, and cassiterite :
1) wolframite ; 2) cassiterite; 3) khlopinite.

Determination of Scandium in Minerals and Ores After Preliminary Chemical Treatment

Although the direct method of determining scandium is fairly rapid, nevertheless the necessity of preparing special standards for each mineral or ore complicates the analysis considerably. It would seem best to separate scandium by coprecipitation with calcium, the rare earths, and thorium.

We chose calcium and thorium as coprecipitants. Chemical treatment was as follows. The mineral (or ores) was brought into solution by an appropriate method. Thorium nitrate or calcium chloride was added to the solution and the oxalates of thorium, scandium, and calcium precipitated with oxalic acid. The excess calcium (or thorium) added brought down the scandium with it. The oxalates of scandium and calcium or thorium were converted into the oxides by calcining. Since the oxides obtained by chemical treatment were of one type, it was then possible to determine scandium in various minerals and ores on the basis of only one set of standards prepared on the basis of calcium or thorium oxides.

Standards were prepared by grinding up calcium oxide or thorium oxide with scandium oxide.

The following conditions were used for obtaining the spectra during determination of scandium in calcium or thorium oxide: 15 mg of the oxides were mixed with 5 mg of graphite powder containing 5% lanthanum oxide, and the whole packed into the crater in the graphite anode. The shape of the electrode is shown in Fig. 1. The upper electrode was sharpened to a conical point. A D.C. arc was used with a current of 10 amperes and a voltage of 180 volts.

Spectra were photographed with the KSA-1 autocollimating quartz spectrograph, or with an average quartz spectrograph ISP-22.

When thorium oxide was used as the base, scandium was determined on the basis of the lines:

Sc II 2552.36 – La II 2610.34

When calcium oxide was used as the base, the following pairs of lines were used:

Sc II 2552.36 – La II 2610.34
Sc II 3353.7 – La II 3376.33

Using this technique of mixing with calcium or thorium oxide, scandium was determined within the concentration range 0.01 to 0.3%. By coprecipitating scandium with calcium or thorium, enrichment of scandium occurs (50 - 100 times) so that it is possible to determine ten thousandths of a percent of scandium.

The spectrochemical method of determining scandium gives results of approximately the same accuracy as the method of direct determination.

During determination of scandium in calcium oxide, the probable error of a single determination is ± 10%, while the error for determination in thorium oxide is ± 11%.

As an illustration of the reliability of the chemical treatment method, we have given in Table 1 a comparison of the results obtained during determination of scandium in beryl after precipitation of scandium with calcium oxalate on the one hand, and direct determination of scandium on the other.

The methods developed have been widely used for the analysis of mineral raw material and process products obtained during scandium extraction.

TABLE 1

Experiment number	Scandium found in %		Exp. no.	Scandium found in %	
	By the direct method	After separation with calcium oxide		By the direct method	After separation with calcium oxide
1	0.10	0.096	9	0.10	0.10
2	0.10	0.10	10	0.10	0.12
3	0.10	0.11	11	0.10	0.11
4	0.10	0.09	12	0.10	0.10
5	0.10	0.08	13	0.10	0.10
6	0.10	0.09	14	0.10	0.09
7	0.10	0.12	15	0.10	0.11
8	0.10	0.11			

TABLE 2

Test material	Sample weight in g	Scandium found, in %	Scandium content, in g	
Starting material	1.86	0.024	0.044	
Undecomposed residue	60	0.01	0.006	0.043
Solution after precipitation of scandium	Not detected			
Calcium oxide	12.0	0.31	0.037	

Table 2 contains the results of a balance experiment on extraction of scandium from mineral raw material, calculated on the basis of the result of spectrographic analysis.

SUMMARY

1. A quantitative spectrographic method has been developed for direct determination (from 0.01 to 0.5%) of scandium in khlopinite, wolframite, cassiterite, and beryl; the probable error of a single determination is ± 6 -12%.

2. A description is given of a universal determination of scandium in various minerals and ores; this method is based on coprecipitation of scandium with the oxalates of calcium or thorium, followed by spectrographic analysis of the oxides obtained; the standards used are based on calcium or thorium oxides; the probable error of a single determination by this technique is ± 10%.

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SEPARATION OF TITANIUM FROM ACCOMPANYING ELEMENTS BY ION-EXCHANGE CHROMATOGRAPHY

PART 2. SEPARATION OF TITANIUM AND CHROMIUM*

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The possibility of separating two ions on a chromatographic column of ion-exchange resin, in one type of solution or another, can be evaluated by means of their distribution coefficients between sorbent and solution; these coefficients are functions of the exchange constant and the constant of complex formation of the ion [1 -6].

The distribution coefficients allow one to choose the conditions for checking chromatographic separation of the ions; this is of great importance for analytical chemistry.

In the present article we have given the results obtained during systematic study of ion-exchange in hydrochloric, sulfuric, and thiocyanic solutions of quadrivalent titanium and trivalent chromium, and also in solutions containing Complexone III. The distributions coefficients of each element were determined between the ion-exchange resin and the corresponding solutions, by shaking an exact amount of ion-exchange resin with a definite volume of test solution, until equilibrium was reached. Afterwards, the amount of element not absorbed by the resin was determined in an aliquot part of the solution [7].

Distribution coefficients were calculated by means of the formula

$$\varphi = \frac{M_1}{M - M_1} \cdot \frac{V}{m},$$

where M_1 is the fraction of the element in the resin; M is the total amount of element contained in the original solution; V is the volume of solution; and m is the weight of resin.

In all experiments V = 60 ml; m = 0.5 g.

The solutions of quadrivalent titanium had a concentration of 1.04×10^{-5} mole/liter, while those of trivalent chromium had a concentration of 1.02×10^{-5} mole/liter; The ion-exchange resins used were the cation-exchange resin SBS and the anion-exchange resin EDE-10. The resins were washed free from impurities before use: resin SBS was converted into the H-form; while resin EDE-10 was used in the Cl^-, SO_4^{2-}, and SCN^- form according to experimental conditions. Distribution coefficients for hydrochloric solutions are given in Table 1.

Results obtained in sulfuric solutions are given in Table 2.

It is thus possible to conclude that quadrivalent titanium and trivalent chromium exhibit almost equal sorbability on the resins studied, in both hydrochloric and sulfuric acid solutions; their sorbability on the cation-exchange resin is not very high in dilute solutions, and falls with increasing acid content (increase in H^+ concentration, formation of anionic complexes); the anion-exchange resin hardly sorbs any of either element from strong acid solutions.

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* For Part 1, see Bull. Moscow State University, Mathematics, Mechanics, Astronomy, Physics, and Chemistry Series 1956, p. 167.

It is of interest to note that the distribution coefficients of trivalent iron between SBS and 0.1 N H_2SO_4 and 0.1 N HCl, are 1932.0 and 1422.0 respectively, which indicates considerable sorbability of iron; consequently, trivalent chromium behaves like titanium and not iron in the solutions studied. The similarity in the sorption properties of titanium and chromium means that they cannot be separated in hydrochloric or sulfuric acid solutions. The distribution coefficients of titanium and chromium were also determined in ammonium thiocyanate solutions at different concentrations of the latter (Table 3).

TABLE 1

Distribution Coefficients φ for Quadrivalent Titanium and Trivalent Chromium in Hydrochloric Acid Solutions on SBS and EDE-10

Normality of HCl	SBS			EDE-10		
	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$
0.1	216.0	168.0	1.28	Not absorbed	Not absorbed	—
0.4	15.6	17.1	0.91	»	»	—
1	10.8	11.6	0.93	»	»	—
4	Not absorbed	Not absorbed	—	»	»	—
12	"	"	—	8.6	19.7	0.44

TABLE 2

Distribution Coefficients φ for Quadrivalent Titanium and Trivalent Chromium in Sulfuric Acid Solutions on SBS and EDE-10

Normality of H_2SO_4	SBS			EDE-10		
	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$
0.1	110.4	108.0	1.02	Not absorbed	Not absorbed	—
1	Not absorbed	9.6	—	»	»	—
4	"	Not absorbed	—	3.9	5.7	0.68
12	»	"	—	15.1	20.5	0.73

TABLE 3

Distribution Coefficients for Quadrivalent Titanium and Trivalent Chromium in Thiocyanate Solutions on SBS and EDE-10 at pH 2.5-3

Molarity of NH_4SCN	SBS			EDE-10		
	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$	φ_{Ti}	φ_{Cr}	$\varphi_{Ti}/\varphi_{Cr}$
$5 \cdot 10^{-3}$	Completely absorbed	Completely absorbed	—	—	—	—
$1,2 \cdot 10^{-2}$	»	2544.0	—	—	6.5	—
$4 \cdot 10^{-2}$	»	552.0	—	9.4	22.2	0.42
0.16	102.0	108.0	0.94	16.5	22.2	0.74
0.7	95.2	98.7	0.96	24.0	37.5	0.64
1.4	72.0	98.7	0.73	24.0	37.6	0.64
5.6	72.0	96.1	0.75	—	—	—

By comparing the distribution coefficients it is possible to conclude that the sorbability of titanium and chromium from thiocyanate solutions is almost the same. Further it is worth noting that the sorbability of titanium and chromium on EDE-10 is insignificant in all the cases we studied.

Complexone III, like other complexones, forms soluble compounds of varying stability with a number of elements. We determined the distribution coefficients of titanium and chromium between the ion-exchange resins and 0.5% Complexone III solutions at various pH values (Table 4).

The sharp difference in sorbability of titanium and chromium from solutions in Complexone III onto the resin enables these elements to be separated.

TABLE 4

Distribution Coefficients φ for Quadrivalent Titanium and Trivalent Chromium in 0.5% Solutions of Complexone III on SBS and EDE-10 at Various pH Values

pH of Complexone III Solution	SBS			EDE-10		
	φ_{Cr}	φ_{Ti}	$\varphi_{Cr}/\varphi_{Ti}$	φ_{Cr}	φ_{Ti}	$\varphi_{Ti}/\varphi_{Cr}$
2.05	1108.0	52.6	21.06	6.0	18.0	3.00
3.14	1108.0	52.5	21.06	5.5	9.5	1.72
4.10	1152.2	52.4	21.90	5.2	7.5	1.44
5.10	1120.5	52.6	21.34	5.8	9.5	1.63

TABLE 5

Chromatographic Separation of Titanium and Chromium on SBS by Means of a 0.5% Solution of Complexone III (pH about 4)

Ratio of Ti : Cr	Ti taken, in mg	ml of Complexone III solution	Ti found, in mg	Cr taken, in mg	Volume of H_2SO_4, in ml	Cr found in mg
1 : 100	0.010	25	0.010	1.012	200	1.000
	0.010	25	0.010	1.012	200	0.992
	0,010	25	0.010	1.012	200	0.998
10 000 : 1	10.080	150	10.080	0.001	50	0.001
	10.080	150	10.067	0.001	50	0.001
	10.080	150	10.071	0.001	50	0.001

We developed the following method of separation. A column (14 cm long and 1.5 cm diameter) is filled with resin SBS in the H-form and eluted with a 0.5% solution of Complexone III (pH about 4); test solution containing titanium and chromium is then introduced into the top of the column; the column is eluted with 0.5% Complexone III solution until all the titanium has been extracted; chromium is removed from the column by means of 4 N H_2SO_4. Results of such separations are given in Table 5.

The separation effected can be regarded as satisfactory.

SUMMARY

Distribution coefficients have been determined for quadrivalent titanium and trivalent chromium between ion-exchange resins (SBS and EDE-10) and 1) solutions of hydrochloric and sulfuric acids of different normalities; 2) solutions of ammonium thiocyanate of varying concentration; 3) a 0.5% solution of Complexone III at various pH values. A method has been developed for the quantitative chromatographic separation of titanium and chromium at ratios of Ti: Cr ranging from 1:100 to 10,000:1 by means of a 0.5% solution of Complexone III.

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DETERMINATION OF THE LOWER OXIDES OF TITANIUM IN THE PRESENCE OF DIVALENT IRON

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Development of analytical methods which would enable one to solve the problem of the form in which titanium is found in slags is of great theoretical and practical interest.

In 1945 Chernomordik [1] developed a method for determining total lower oxides of titanium in the absence of ferrous iron. The scheme of analysis suggested by this author is not suitable for industrial slags containing divalent iron. The object of the work described here was to develop methods for determining reduced titanium and divalent iron.

In our work we used preparations* obtained by means of the reaction: $3TiO_2 + Ti = 2Ti_2O_3$. The extent to which the titanium has been reduced in the preparations was established from the increase in weight of the products calcined to a constant weight at 900° in an oxygen stream. If the preparations obtained had been the pure oxide Ti_2O_3, the increase in weight should be 11.1%. Actually, the increase in weight of the first preparation was 20.8% while that of the second and third preparations were 12.3% and 10.5% respectively. Thus preparations 1 and 2 contained metallic titanium and possibly TiO in addition to Ti_2O_3. Preparation 3 was obviously a mixture of Ti_2O_3 and TiO_2.

In order to determine total lower titanium oxides, the preparations were dissolved in acid in the presence of an oxidizing agent (quinquevalent vanadium, quadrivalent cerium, or trivalent iron).

Determination of Reduced Titanium (Ti_2O_3) By Means of Quinquevalent Vanadium

A 0.1 g aliquot of preparation 1 was decomposed in a mixture of 10 ml HF and 5 ml H_2SO_4 (sp.gr.1.84) in a platinum basin, in the presence of a sulfuric acid solution of vanadium pentoxide. Since the normal potential of the system VO_2^+ VO^{2+} is + 1.0 volt, while the normal potential of the system Ti^{IV}/Ti^{III} is +0.10 volt, then, in solution, trivalent titanium reacts with quinquevalent vanadium. The quadrivalent vanadium compound formed $(VO)_2(SO_4)_2$ exhibits high stability, so that it is possible to work in the absence of an inert gas. Excess quinquevalent vanadium was titrated with 0.05 N solution of Mohr's salt.

A blank must be carried out at the same time.

The amount of Ti_2O_3 was calculated by means of the formula;

$$\%\ Ti_2O_3 = \frac{143.8 \cdot N\ (V_1 - V_2)}{2 \cdot 1000\ n}\ 100, \qquad (1)$$

where N is the normality of the Mohr's salt solution; V_1 is the volume of Mohr's salt solution used in the blank; V_2 the volume of the same solution used for titrating excess vanadium pentoxide; and n is the weight of sample.

Results of these determinations are given in Table 1.

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* The preparations of reduced titanium were presented by the Laboratory of Metallurgical Raw Materials (T.P. Ukolova).

TABLE 1

Determination of Reduced Titanium ($\%Ti_2O_3$) in Preparation 1 and in Slag

	Fraction I, fine crystals	Fraction II, medium size crystals	Fraction III, large crystals	Slag
	91.03	95.43	95.32	8.66
	92.83	95.59	97.26	8.16
				8.19
	91.97	95.35	96.77	8.13
				8.19
	91.70	95.94		8.19
		94.51		8.60
Mean	91.88±0.51	95.36±0.35	96.45±0.75	8.30±0.18

Determination of Reduced Titanium by Means of Quadrivalent Cerium

An aliquot of 0.1 g of preparation 2 was broken down in a mixture of 30 ml H_3PO_4 (sp. gr 1.7) and 5 ml H_2SO_4 (sp.gr. 1.84) in the presence of excess cerium sulfate. $Ce(SO_4)_2$ was first introduced into the reaction flask, H_2SO_4 was then added, and last of all H_3PO_4 introduced. This order of adding the reagents prevents deposition of a precipitate of cerium phosphate. The material was decomposed by heating for 15-30 minutes. Quadrivalent cerium which possesses a high potential of + 1.44 volt, oxidized Ti^{III} to Ti^{IV}, and was reduced to the stable trivalent state. When decomposition was complete, the solution was cooled to room temperature, and diluted with distilled water to 100 ml. Excess $Ce(SO_4)_2$ was back titrated with the solution of Mohr's salt in the presence of phenylanthranilic acid. A blank test was carried out under the same conditions.

The results obtained are given in Table 2.

As the results show, agreement between replicates is good.

The results obtained agree with the results obtained for the same sample using quinquevalent vanadium.

Determination of Reduced Titanium Ti_2O_3 By Means of Trivalent Iron

Decomposition of preparation 3 was carried out by heating in a palladium flask in a CO_2 stream. A mixture of 15 ml H_2SO_4 1:3, and 5 ml HF was used for the decomposition. Iron alum was taken in sufficient amount to oxidize all the reduced titanium. Trivalent iron oxidizes Ti^{III} to Ti^{IV}, since $E_{Fe^{3+}/Fe^{2+}} = +0.77v$; $E_{Ti^{IV}/Ti^{III}} = +0.10$ volt. When decomposition was complete (20-30 minutes), flask plus solution were cooled without stopping the CO_2 stream, and the cooled solution transferred to a 250 ml flask into which 10 ml of a saturated aqueous solution of boric acid had been introduced beforehand for complexing fluoride ions. The solution was diluted with distilled water to 100 ml and ferrous iron titrated with 0.05 N $KMnO_4$.

The amount of Ti_2O_3 was calculated by means of the formula:

$$\%\,Ti_2O_3 = \frac{T_{Ti_2O_3}\cdot V}{n}\,100, \qquad (2)$$

where $T_{Ti_2O_3}$ is the titer of $KMnO_4$ solution expressed in terms of Ti_2O_3; V is the volume of $KMnO_4$ solution equivalent to Ti_2O_3; n is the weight of sample. Results of these determinations are given in Table 3.

The results obtained by means of trivalent iron and quinquevalent vanadium show good reproducibility and agree with each other with an accuracy of one relative percent; this is fully acceptable for determination of such large amounts of titanium.

When reduced titanium is to be determined in a slag containing ferrous iron, the quinquevalent vanadium and quadrivalent cerium will, in such a case, be reduced by the divalent iron. Accordingly, in applying

the methods described to slags, we shall determine total reduced titanium and divalent iron. Consequently, the second part of the work was devoted to developing a method for determining ferrous iron in the presence of trivalent titanium.

TABLE 2

Determination of Reduced Titanium ($\%\ Ti_2O_3$) in Preparation 2

Oxidizing agent Ce^{IV}	Oxidizing agent V^V
87.79	87.94
88.15	87.92
87.31	87.88
87.88	87.06
Mean 87.77±0.24	87.70±0.32

TABLE 3

Determination of Reduced Titanium Ti_2O_3 in Preparation 3

Oxidizing agent Fe^{III}	Oxidizing agent V^V
93.09	94.91
92.51	94.62
94.77	94.84
93.97	94.61
93.35	93.24
94.08	95.24
94.40	95.24
93.33	—
92.50	—
Mean 93.55±0.66	94.67±0.44

As a basis of the method for determining FeO in the presence of Ti_2O_3, use was made of the difference in their stability during boiling in a mixture of HF and H_2SO_4 in a CO_2 stream. Under these conditions divalent iron is stable, while Ti_2O_3 is oxidized. This fact can be explained from the point of view of the theory of oxidation-reduction processes and the theory of specific complex formation.

F^- ions complex Ti^{IV} ions present in solution into a stable complex, and depress the concentration of the oxidized form to a negligible value. The potential of the system is shifted sharply to the negative side.

According to published results [2], $E_{Ti^{IV}/Ti^{III}} = +0.10$ volt drops in the presence of HF to $E = - -0.124$ volt. Consequently, the reduced titanium becomes very unstable, and most of it, if not all, is oxidized. Therefore, on decomposing slag in a mixture of HF and H_2SO_4, a solution is obtained which contains divalent iron and small amounts of reduced titanium which is oxidized by one of the following methods.

1. Oxidation of Trivalent Titanium by Aeration. Titanium and iron in various proportions, and in the form of sulfuric acid solutions of their salts, were introduced into a 500 ml flask. The volume of the solution was adjusted to 100 ml with an acidity of 2N with respect to H_2SO_4. Air was bubbled through the solution for 30 minutes. Under such conditions trivalent titanium was oxidized; the iron was back titrated with $Ce(SO_4)_2$ or NH_4VO_3 in the presence of phenylanthranilic acid.

Results are given in Table 4.

TABLE 4

Determination of Divalent Iron in the Presence of Ti^{III}

Iron titrated with $Ce(SO_4)_2$				Iron titrated with NH_4VO_3			
Ti/Fe	Fe taken, in g	Fe found, in g	Δ in g	Ti/Fe	Fe taken, in g	Fe found, in g	Δ in g
5 : 1	0.0140	0.0145	+0.0005	3 : 2	0.0280	0.0294	+0.0014
4 : 1	0.0140	0.0146	+0.0006	1 : 1	0.0280	0.0289	+0.0009
5 : 2	0.0140	0.0146	+0.0006	1 : 2	0.0280	0.0289	+0.0009
2 : 1	0.0140	0.0145	+0.0005	1 : 4	0.0560	0.0574	+0.0014
				1 : 8	0.0560	0.0574	+0.0014
				12 : 1	0.0012	0.0013	+0.0001
				5 : 2	0.0056	0.0055	−0.0001

The somewhat high results are a consequence of the fact that the sulfuric acid solution of ferrous salt contained small amounts of trivalent iron, which reacted with trivalent titanium to give an additional amount of ferrous iron. When the sulfuric acid solution of ferrous salt was passed through a bismuth reducer before aeration, so that the small amounts of Fe^{3+} were reduced, the error amounted to ± 0.1 mg.

TABLE 5
Determination of Divalent Iron in the Presence of Ti^{III}

Ti/Fe	Fe taken, in g	Fe found, in g	Δ in g
12 : 1	0.0012	0.0013	+0.0001
5 : 2	0.0056	0.0056	0.0000
1 : 2	0.0018	0.0016	−0.0002

2. Titration of Residual Titanium with $KMnO_4$ in the Presence of Na_2WO_4 as Indicator.

From a comparison of the values of the normal potentials $E_{WO_3/WO^{3+}}$ = + 0.26 v, $E_{Ti^{IV}/Ti^{III}}$ = = + 0.10 volt, it follows that tungsten can be reduced in the presence of titanium. Reduction proceeds readily in 2N H_2SO_4 in the presence of 10-20 ml phosphoric acid (sp.gr. 1.7). The blue colored reduction product was titrated with $KMnO_4$, and divalent iron was then titrated with NH_4VO_3 in the presence of phenylanthranilic acid.

Results of such determinations are given in Table 5. As the results show the experimental error in this case is low and amounts to ± 0.1 mg.

3. Titration of Residual Titanium with Cerium Sulfate Using Cacotheline as Indicator (E = +0.46 volt). The color of the solution changes from violet to yellow. After titanium has been titrated, the iron was titrated with cerium sulfate in the presence of phenylanthranilic acid. The solution was 2 N with respect to H_2SO_4.

Experimental results are given in Table 6.

TABLE 6
Determination of Divalent Iron in the Presence of Ti^{III}

Ti/Fe	Fe taken, in g	Fe found, in g	Δ in g
5 : 1	0.0083	0.0071	−0.0012
3 : 1	0.0131	0.0123	−0.0008
1 : 1	0.0261	0.0254	−0.0007
1 : 2	0.0261	0.0249	−0.0012
1 : 4	0.0261	0.0254	−0.0007
1 : 8	0.0521	0.0507	−0.0014

TABLE 7
Determination of Reduced Titanium and Ferrous Iron in Slags

Sample number	Ti_2O_3, in %	FeO, in %
7001	18.33±0.28	8.83±0.08
7002	25.52±0.29	5.38±0.06
7144	76.14	4.14
7041	67.36	1.76
7145	2.56	41.02
3353	38.16	0.45

The small negative error does not exceed 1.5 mg. All the three variants for determining divalent iron can be used; the best of the three is, however, the second variant both from the point of view of simplicity and rapidity. On the basis of the results obtained, the following scheme can be suggested for analyzing materials containing reduced titanium and ferrous iron: total lower oxides of titanium and ferrous iron are determined in one aliquot; ferrous iron is determined in a second aliquot.

The amount of Ti_2O_3 is calculated by means of the formula:

$$\% \ Ti_2O_3 = \frac{143.8 \ (N_1V_1 - N_2V_2)}{2 \cdot 1000 \ n} \ 100, \qquad (3)$$

where N_1 is the normality of the solution of Mohr's salt; N_2 is the normality of the NH_4VO_3 solution which is used for titrating FeO; V_1 is the volume of Mohr's salt solution equivalent to total Ti_2O_3 and FeO; V_2 is the volume of NH_4VO_3 solution used for titrating divalent iron; and n is the weight of sample.

The method developed was used for analyzing slags containing Ti_2O_3 and FeO.

Results are given in Table 7.

The author wishes to thank A.I. Ponomarev and B.N. Melentev for advice and help in preparing this article for publication.

SUMMARY

1. A method has been developed for determining total lower oxides of titanium in slags containing FeO. The accuracy of the method (mean deviation of a series of tests) does not exceed 1.5% (relative percentage); this is obviously good enough for solving the question of the state of titanium in slags.

2. Since reduced titanium is extremely unstable on heating, it is therefore expedient to decompose the slags in the presence of excess oxidizing agents: V_2O_5, CeO_2, and Fe_2O_3.

Determinations carried out by means of any of the oxidizing agents mentioned give satisfactory reproducibility.

3. The best of the three methods developed for determining FeO in the presence of titanium is the one involving Na_2WO_4.

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COMPLEXOMETRIC DETERMINATION OF BISMUTH WITH 1-(2-PYRIDYLAZO)-2-NAPHTHOL AS INDICATOR*

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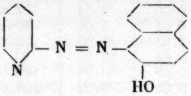
The complex compound formed between bismuth and ethylenediaminetetracetic acid is still stable at pH 1-2, while the compounds of most other elements either practically completely, or very strongly dissociate at such a pH. The discovery of a specific chemical indicator for the bismuth ion at pH about 1, solves the question of a simple and rapid quantitative method of determining bismuth in the presence of many other elements which accompanies it in natural and industrial materials. At the moment [1], there are no titrimetric methods of determining bismuth which completely satisfy the requirements of production control for lead and other metals. Complexometric methods for titrating bismuth which have been published recently [2-9] ** have not found practical application for a number of reasons, although the amperometric method [2], and the method involving pyrocatechin violet [7, 8] as indicator deserve more attention. Pyrogallol red may acquire practical significance as an indicator for the complexometric titration of bismuth at a pH of 2-3 [9].

In the present article it is shown that 1-(2-pyridylazo)-2-naphthol,



which can be comparatively readily synthesized by A.E. Chichibabin's method [11] of diazotizing α-aminopyridine, is a very good selective indicator for titrating the bismuth ion in acid solution (pH 1) with a solution of disodium ethylenediaminetetracetate, in the presence of large amounts of lead and many other elements. 1-(2-pyridylazo)-2-naphthol which has a yellow color gives with bismuth ions, and also with ions of divalent copper and iron, at a pH of about 1, intensely rose colored complexes [12]. At higher pH values, the azo dye gives red complexes not only with bismuth, but also with cadmium, divalent copper, platinum, uranium, divalent mercury, thorium, lead, di- and trivalent iron, nickel, zinc, lanthanum, quadrivalent cerium, indium, scandium, europium, and gives green complexes with palladium and cobalt [12]; thus the azo dye loses its specificity as an indicator for bismuth.

1-(2-pyridylazo)-2-naphthol has already been used as a complexometric indicator during direct titration of zinc and cadmium at pH 5-7, and also of copper in acetic acid solution [12], and indium at pH 2.3 - 2.5 or at pH 7-8 [13]. Flaschka and Abdine [14] have determined nickel, cobalt, zinc, cadmium, copper, lead and iron, by adding excess disodium ethyelenediaminetetracetate, and back titrating it in acetic acid media with a copper salt, using the compound mentioned as indicator. Cheng and Williams [15] determined scandium in a similar way (at pH 2.5).

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* N. V. Bychkova participated in the experimental part.

** A review of earlier papers is given in Prshibil's monograph [10].

The high specificity of the reaction between bismuth ions and ethylenediaminetetracetic acid at pH 1, coupled with the high specificity of 1-(2-pyridylazo)-2-naphthol as indicator for bismuth ions, also at a pH of about 1, enables one to carry out a very selective determination of this element. The procedure for determining bismuth is exceedingly simple.

To 1.00 - 10.0 ml of a 0.05 - 0.01 M nitric acid solution of bismuth nitrate is added ammonia so as to adjust the pH to 1.0 (Universal indicator paper); this is followed by 1-2 drops of a 0.1% solution of the indicator in methanol, and the whole titrated with a 0.01 or 0.05 M solution of sodium ethylenediaminetetracetate (Complexone III) until the color changes from rose to yellow on addition of one drop of titrant. Standard solutions of disodium ethylenediaminetetracetate are prepared by dissolving the exact amount of $Na_2H_2C_{10}H_{12}O_8 \cdot N_2 \cdot 2H_2O$ after purification of the salt by the method of Blaedel and Knight [16]; the latter method ensures preparation of material of high purity.

Results of some bismuth determinations are given in Table 1.

TABLE 1

Titration of Bismuth with a Solution of Disodium Ethylenediaminetetracetate

Amount taken			Titrant solution used		Bi found, in mg	Error	
$Bi(NO_3)_2$ solution							
Molarity	In ml	Bi, in mg	Molarity	In ml		Absolute, in mg Bi	In %
0.05	1.00	10.45	0.05	1.01	10.55	+0.1	+0.95
0.01	1.00	2.09	0.01	1.00	2.09	0	0
0.01	1.00	2.09	0.01	1.04	2.17	+0.08	+3.6
0.05	2.00	20.90	0.05	1.88	19.65	—1.25	—6.0
0.01	2.00	4.18	0.01	2.00	4.18	0	0
0.05	2.00	20.90	0.05	2.02	21.11	+0.21	+1.0
0.01	2.00	4.18	0.01	2.00	4.18	0	0
0.01	5.00	10.45	0.01	5.05	10.55	+0.1	+0.9
0.01	5.00	10.45	0.01	5.01	10.47	+0.02	+0.18
0.05	5.00	52.25	0.05	4.93	52.01	—0.24	—0.46
0.05	5.00	52.25	0.05	4.95	51.73	—0.52	—1.0
0.05	5.00	52.25	0.05	5.04	52.67	+0.42	+0.8
0.01	5.00	10.45	0.01	5.00	10.45	0	0
0.01	10.00	20.90	0.01	10.02	20.94	+0.04	+0.2
0.01	10.00	20.90	0.01	10.10	21.11	+0.21	+1.0
0.05	10.00	104.5	0.05	10.05	105.02	+0.52	+0.5
0.05	10.00	104.5	0.05	9.92	103.66	—0.84	—0.8

Experimental error does not exceed the limits imposed by accuracy with which volume of titrant can be measured on the micro-buret used. When macro amounts of bismuth are determined, the experimental error is of the normal order for titrimetric methods.

Large amounts of lead do not interfere with bismuth determination; neither do cadmium, zinc, strontium, barium, calcium, magnesium, aluminum, indium, gallium, silver, manganese (Table 2), and other elements. They do not form complexes with ethylenediaminetetracetate and with 1-(2-pyridylazo)-2-naphthol at pH 1-2; traces of copper, cobalt, nickel, chromium, and mercury do not interfere either.

Bismuth can also be titrated at pH > 2.5 - 3.2; under these conditions, however, the specificity of bismuth determination decreases somewhat. Titration of bismuth in tartrate or pyrophosphate solutions at high pH values cannot be realized, because under such conditions, bismuth does not give a rose colored complex with the indicator (as a result of the high stability of the tartrate complex of bismuth).

Thanks to the simplicity of the technique, its high degree of accuracy, its selectivity, and the possibility of determining small amounts of bismuth, the method can be used for production control, e.g. of metallic lead.

During a study of the possibility of a complexometric determination of bismuth by means of hexamethylenediaminetetracetic acid

$$(HOOCH_2C)_2=N-[CH_2]_6-N=(CH_2COOH)_2$$

and disodium benzohydrylaminediacetic acid

$$C_6H_5-CH(-C_6H_5)-N=(CH_2COONa)_2,$$

synthesized recently [17], it was established that these materials do not form stable complexes with bismuth in weakly acidic (pH 2.0-3.5) and weakly alkaline (pH 9 and higher) solutions; they do not mask bismuth with respect to various reagents. On addition of these reagents to a solution of a bismuth salt, followed by excess dilute ammonia, there is formed a white precipitate of a basic salt which does not dissolve; under similar conditions, but using disodium ethylenediaminetetracetate, stable transparent solutions are obtained. Further, the half wave potential of the bismuth tartrate complex at pH 8-9 does not alter on adding hexamethylenediaminetetracetic acid and adjusting the pH to its original value. That hexamethylenediaminetetracetic acid is incapable of forming stable complexes with bismuth is confirmed by an analysis of the results obtained by R.P. Lastovsky and coworkers [17]. This fact is also in agreement with the results obtained by Schwarzenbach and Ackermann [18], who showed that polymethylenediaminetetracetic acids

$$(HOOC-CH_2)_2=N-(CH_2)_n-N=(CH_2-COOH)_2,$$

where n = 3 - 5, form less stable complexes with metals than ethylenediamine. Thus, hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate cannot be used for titrating bismuth. It should be noted that even if they could form stable complexes with the bismuth ion at high pH values (in the presence of tartrates), titration of bismuth with 1-(2-pyridylazo)-2-naphthol would still be out of the question, since the indicator itself, as pointed out already, is incapable of forming a complex with bismuth ions under such conditions.

TABLE 2

Determination of Bismuth in the Presence of Other Elements (2.09 mg of Bi was taken in each case, pH 1.0 - 1.4)

Element (Me) added in mg	Ratio Bi: Me	Bi found, in mg	Error	
			In mg	In %
350 Pb	1 : 170	2.21	+0.12	+5.7
350 Pb	1 : 170	2.11	+0.02	+0.95
650 Pb	1 : 340	2.11	+0.02	+0.95
980 Pb	1 : 470	2.17	+0.08	+3.8
520 Cd	1 : 250	2.21	+0.12	+5.4
410 Zn	1 : 200	2.23	+0.14	+6.2
640 Ba	1 : 310	2.25	+0.16	+7.1
880 Sr	1 : 880	2.21	+0.12	+5.4
1300 Ca	1 : 620	2.29	+0.20	+9.0
230 Mg	1 : 100	2.23	+0.14	+6.2

The author wishes to thank R.P. Lastovsky for his gift of samples of hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate to carry out this work.

SUMMARY

1-(2-pyridylazo)-2-naphthol is a very good indicator for direct titration of bismuth in acid solution (pH 1) with disodium ethylenediaminetetracetate in the presence of large amounts of lead, cadmium, zinc, and other elements. Hexamethylenediaminetetracetic acid and disodium benzhydrylaminediacetate are not suitable for complexometric determination of bismuth, since they do not form stable complexes with bismuth.

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AMPEROMETRIC TITRATION OF PALLADIUM BY MEANS OF CERTAIN ORGANIC REAGENTS USING A ROTATING PLATINUM ELECTRODE

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A few papers [1-6] have been devoted to polarographic determination of palladium on the dropping mercury electrode. We have demonstrated that it is possible to use both the stationary and rotating platinum electrode for this purpose [7]. The height of the palladium wave on the rotating electrode [7] is proportional to palladium concentration in solution, and is suitable for determining palladium not only polarographically, but also amperometrically.

Amperometric titration of palladium (and the platinum group of metals in general) has been carried out by Kolthoff and Langer [8], and by Tomicek and coworkers [5], on a dropping mercury electrode. In the present article we shall describe results of studies of the possibility of carrying out amperometric titration of palladium with certain other organic reagents, using the rotating platinum electrode described earlier [7].

Titration was carried out as follows. Into a 10 ml standard flask was introduced a standard solution of palladium chloride; this was made up to volume with a solution of supporting electrolyte (0.1 N $NaNO_3$); this solution was transferred to a polarographic cell and nitrogen bubbled through it to expel oxygen. The motor was then switched on and on applying an emf of 0.9 - 1.0 volt, reagent solution was added from a micro-buret. Current was measured 45 seconds after addition of each portion of reagent. Nitrogen was slowly passed through the solution during titration. Because of the vigorous action of the rotating electrode (800 revolution / minute), the passage of nitrogen did not affect the galvanometer readings.

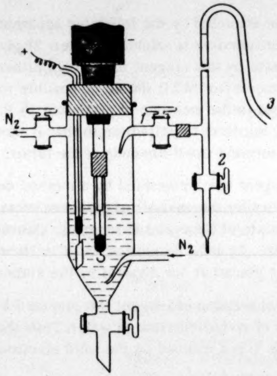

Fig. 1.

For amperometric titration with a rotating platinum electrode, and a mercury seal for preventing contact between solution and the air, the scheme shown diagramatically in Fig. 1 proved useful for connecting the micro-buret to the cell (Fig. 1).

The micro-buret was made in such a way that by placing the beaker plus solution under its lower tip, it is possible, by opening tap 2, for sucking air through tube 3, to fill the buret. Then, using this same tap 2, the level of the liquid is adjusted to zero. Having opened tap 1 titration can then be carried out. This type of setup ensures that the apparatus is hermetically sealed, and means that work can be carried on without interruption, however long the titration lasts.

The buret can be connected to tap 1 by means of a length of rubber tubing, so that it can be readily disconnected, when necessary, for washing, etc.

1. Titration with α-Nitroso-β-naphthol

Schmidt [9] has used α-nitroso-β-naphthol for separating palladium from platinum and rhodium, while Wunder and Thuringer [10] have used it for separating palladium from copper and iron. Kolthoff and Langer [8] have used this reagent for amperometric titration of cobalt, copper, and palladium.

Since the authors mentioned obtained completely satisfactory results with the dropping mercury electrode, we tried to carry out such a titration using a rotating electrode. The preparation at our disposal was recrystallized from alcohol. An approximately 0.01 M solution of reagent was prepared from this purified product by dissolving an aliquot in 50% acetic acid.

The experiments carried out showed that using 0.1 M $NaNO_3$, as well as 0.1 M CH_3COOH and 0.1 M CH_3COONa as supporting electrolytes, the solution of α-nitroso-β-naphthol was not reduced on a solid electrode.

Amperometric titration with α-nitroso-β-naphthol in a supporting electrolyte of $NaNO_3$ did not yield satisfactory results when the rotating electrode was used. Determination of the reaction end point was exceedingly difficult, so that the results obtained varied.

2. Titration with β-Furildioxime

α-furildioxime is one of the organic reagents which has started attracting the attention of analysts in recent years [11-15]. Pshenitsyn and Nekrasova [16] have established that palladium is precipitated by α-furildioxime at HCl concentrations in the solution not exceeding 0.5% by weight.

There is no published information regarding the possibility of using α-furildioxime for determining palladium amperometrically; accordingly, we checked on the possibility of carrying out such determination on a solid rotating electrode.

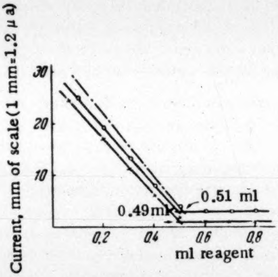

Fig. 2.

We were attracted by the following apparent advantages: 1) α-furildioxime is soluble in water; 2) platinum is not precipitate by this reagent in the cold, either in acid or in neutral media (so that it should be possible to determine palladium in the presence of platinum); 3) the reagent is fairly sensitive to palladium, so that it should be possible to determine small amounts of the latter.

The reagent was synthesized by a method developed in the laboratory for the analysis of platinum metals of the Kurnakov Institute of General and Inorganic Chemistry, Acad. Sci. USSR, by N.K. Pshenitsyn and G.A. Nekrasova, and was kindly placed at our disposal by the authors.

A 0.01 M solution of reagent was prepared by dissolving an aliquot of α-furildioxime in water. Tests showed that α-furildioxime is not reduced on the solid electrode.

In Fig. 2 are shown three curves obtained during replicate titration of the same sample of palladium with the α-furildioxime solution. As can be seen from these curves, good reproducibility was obtained during replicate titrations. Table 1 contains results which confirm this for other palladium concentrations. The deviation of a single determination from the mean did not exceed 2%.

During titration of various amounts of palladium, a proportionality was detected between the volume of α-furildioxime solution and the concentration of palladium in solution (Fig. 3).

The exact concentration of the α-furildioxime solution could be established by titrating various volumes of a standard palladium solution whose concentration had been established gravimetrically (Table 2). For calculating α-furildioxime concentration one can make use of the formula for the reagent $(C_3H_3C : NOH)_2 \cdot H_2O$ (Mol.wt. 238.20) and the reaction equation, according to which two molecules of α-furildioxime react with one molecule of palladium.

TABLE 1

Reproducibility of the Results of Titrating Palladium with α-Furildioxime

Palladium taken		Ml of α-furildioxime solution used for titration
In ml	In mg	
0.5	0.24	0.36
0.5	0.24	0.35
0.5	0.24	0.36
0.5	0.24	0.37
0.5	0.24	0.36
0.3	0.14	0.20
0.3	0.14	0.21
0.3	0.14	0.21
0.7	0.34*	

* See Fig. 2

TABLE 2

Determination of Concentrartion of α-Furildioxime Solution

Palladium taken, in mg	Ml of α-furildioxime solution used for titration	α-furildioxime found	
		mg/ml	Mole/liter
0.24	0.36	0.298	0.0125
0.34	0.50	0.303	0.0127
0.43	0.63	0.304	0.0128
0.14	0.21	0.297	0.0125
	Mean	0.300	0.0126

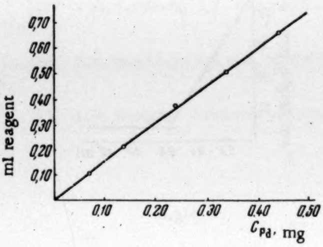

Fig. 3.

It was found in this way that each ml of titrant solution α-furildioxime titrates 0.067 mg palladium. Using these results, the accuracy of the amperometric titration of palladium was checked (Table 3).

3. The Possibility of Using Some Other Organic Reagents

In addition to α-furildioxime we examined the possibility of carrying out amperometric titrations of palladium with some other reagents, in particular with dimethylglyoxime.

Preliminary experiments which we carried out with the rotating electrode showed that dimethylglyoxime, like other oximes which we tested (α-furildioxime, β-furfuraldoxime, and benzoinoxime), is not reduced on a solid electrode either in aqueous or alcohol solutions. In Fig. 4 are shown titration curves for palladium with an alcohol and an aqueous solution of dimethylglyoxime, respectively. As is evident from Fig. 4, the titration curve is similar to those obtained with α-furil dioxime, while the end point can be determined fairly accurately; the accuracy of titration with an aqueous solution is higher than that for titration with an alcohol solution of the oxime.

TABLE 3

Palladium Determination

Palladium taken, in mg	α-furildioxime used, in ml	Palladium found, in mg	Error	
			Absolute, in mg	Relative, in %
0.288	0.42	0.281	—0.007	—2.5
0.384	0.57	0.381	—0.003	—0.8
0.240	0.37	0.248	+0.008	+3.3
0.096	0.15	0.100	+0.004	+4.1
0.480	0.71	0.476	—0.004	—0.9
0.530	0.80	0.536	20.006	+1.1
0.576	0.85	0.569	—0.007	—1.3
0.192	0.30	0.201	—0.009	+4.6
0.192	0.28	0.187	—0.005	—2.3
		Mean		+2.3

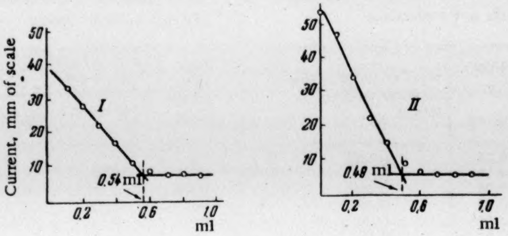

Fig. 4.

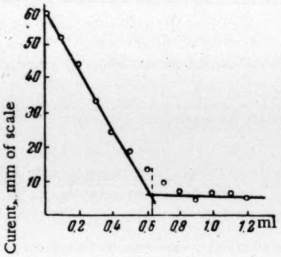

Fig.5

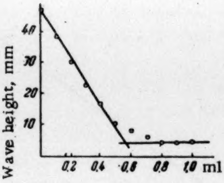

Fig.6.

The sodium salt of dimethylglyoxime, which is readily soluble in water, was used successfully instead of dimethylglyoxime itself, which is only sparingly soluble in water (Fig. 5). The salt was prepared by dissolving the calculated amount of dimethylglyoxime in NaOH, followed by precipitation with alcohol [17].

In Fig. 6 are shown examples of titration of palladium with β-furfuraldoxime and o-hydroxyquinoline, respectively.

SUMMARY

1. A study has been made of the possibility of using a solid rotating platinum electrode for amperometric titration of palladium with some organic reagents.

2. It has been shown that α-furildioxime can be used for amperometric determination of palladium with an accuracy of 2-3% at concentrations in solution ranging from 10^{-4} to 10^{-2} M.

3. It has been shown that it is possible to use some other organic reagents (an alcoholic solution of dimethylglyoxime, aqueous solutions of sodium dimethylglyoximate, dimethylglyoxime, and β-furfuraldoxime, and an acetic solution of 8-hydroxyquinoline), for amperometric determination of palladium.

4. In contrast to the dropping mercury electrode, titration of palladium with α-nitroso-β-naphthol on a solid rotating electrode does not give satisfactory results.

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A TITRIMETRIC METHOD FOR DETERMINING CHLORIDE, BROMIDE, AND IODIDE IN THEIR MIXTURES

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Gravimetric and titrimetric methods are widely used for determining large amounts of the halides in their mixtures. Bekk [1]. developed a gravimetric method based on precipitation of the halides by Ag^+. Friedheim and Meyer [2], after appropriate treatment of the solution, determined I^- and Br^- ions by titration with $Na_2S_2O_3$; the chloride ion is precipitated with Ag^+ and is determined gravimetrically.

Berg [3,4] has described a titrimetric method for determining the three halides in mixtures. According to this technique I^- is titrated with potassium iodate in sulfuric acid solution in the presence of acetone. The ion which is liberated reacts with acetone to form undissociated iodoacetone. Total $Br^- + Cl^-$ is determined by the Volhard method. Cl^- is then determined on a separate aliquot containing Cl^-, Br^-, and I^-; for this purpose I^- and Br^- ions are oxidized with potassium bromate, after complexing free I_2 and Br_2 by acetone; Cl^- is determined by the Volhard method, or if the content of Cl^- is low it is determined nephelometrically. The amount of Br^- is found by difference. Mitchell and Ward [3] obtained high results when they used this method for I^- and Br^-. Alpine [6] explains the high results obtained during determination of Cl^- by hydrolysis of bromo- and iodoacetone.

According to Berg's results, the loss of Cl^- as a result of oxidation by bromate may vary from 2 to 40% according to the duration of interaction and halide concentration.

All the indirect methods described above involve many operations, are complicated and difficult, are characterized by a long time for carrying them out, and in the end give insufficiently accurate results [5].

On the basis of our work we have succeeded in improving Berg's titrimetric method – determination of large amounts of halide ions in their mixtures – and have made it simple, accurate, and rapid. Halide ions are determined successively in one aliquot.

Into a 100-200 ml Erlenmeyer flask were introduced by means of pipets 5 or 10 ml each of 0.01 or 0.10 N KI, 0.02 or 0.10 N KCl, and 0.20 N KBr. 15 ml of acetone was then added and was followed by 3-5 ml of H_2SO_4 (1:3); the solution should be colorless when this is done. The total concentration of iodide before titration, as a result of dilution, should be 0.001 or 0.01 N respectively, while the H_2SO_4 concentration should be 0.8 - 1.3 N.

I^- was titrated with 0.01 or 0.10 N KIO_3. The iodine liberated reacted with acetone. Solutions containing 0.001 N KI decolorized periodically, while solution containing 0.01 N KI remained colored and only became colorless towards the end of titration. Titration was then continued, the two or three extra drops of KIO_3 necessary being added carefully. The color change in various instances from yellow to colorless or in the opposite direction, was very clearly marked. At the equivalence point for the oxidation of I^-, the solution remained colorless until the addition of the last drop of KIO_3. One or two drops of KIO_3 in excess was sufficient to guarantee complete precipitation of I^-. At H_2SO_4 concentration of 0.8 - 1.3 N, only I^- was oxidized by iodate; Cl^- and Br^- remained in solution.

Br^- was determined by adding 15 ml of H_2SO_4 (2:1) to the solution with agitation. The total acid concentration of the solution was then 6.7 - 7.30 N, while bromide concentration was 0.018 N. Br^- was determined by titration with 0.40 N KIO_3 in the solution which was still warm after addition of H_2SO_4; the KIO_3 was added dropwise. Under these conditions only Br^- was oxidized; the Br^-, together with the iodine formed during reduction of iodate, colored the solution yellow; the yellow color, however, disappeared quickly as a result of reaction between halides and acetone.

At the equivalence point for oxidation of Br^-, the last drop of KIO_3 did not cause coloring of the solution. 2-3 drops of iodate in excess was sufficient to guarantee complete oxidation of Br^-.

The solution was cooled to room temperature and Cl^- determined. The smallest initial concentration of chloride which could be determined titrimetrically was 0.0017 N. At Cl^- concentrations of this order and higher, Cl^- was determined by the Volhard method, while at lower concentration it was determined nephelometrically. Results of such determinations are given in Tables 1 and 2.

TABLE 1

0.0100 N KIO_3 Was Used for Titrating I^-, While 0.400 N KIO_3 Was Used for Titrating Br^-

Amount taken in ml			Found, in ml		
0.0100 *N* KI	0.200*N* KBr	0.0200*N* KCl	0.0100*N* KI	0.0200*N* KBr	0.200*N* KCl
5.0	5.0	5.0	4.95	4.90	4.85
5.0	5.0	5.0	5.00	4.92	4.94
5.0	5.0	5.0	5.00	5.00	5.00
10.0	10.0	10.0	9.94	9.95	9.85
10.0	10.0	10.0	10.00	10.00	10.00
10.0	10.0	10.0	10.05	10.00	10.05

TABLE 2

0.100 N KIO_3 Was Used for Titrating I^-, While 0.400 N KIO_3 Was Used for Titrating Br^-

Amount taken, in ml			Found, in ml		
0.100*N* KI	0.200*N* KBr	0.100*N* KCl	0.100*N* KI	0.200*N* KBr	0.100*N* KCl
5.0	5.0	5.0	4.96	5.00	5.09
5.0	5.0	5.0	5.00	5.10	4.98
5.0	5.0	5.0	5.05	5.08	5.10
10.0	10.0	10.0	10.05	9.80	10.14
10.0	10.0	10.0	10.15	10.12	10.01
10.0	10.0	10.0	10.20	10,00	9.91

SUMMARY

1. A method has been developed for titrimetric determination of I^-, Br^-, and Cl^- in their mixtures. I^- and Br^- are titrated with potassium iodate, while Cl^- is titrated by the Volhard method.

The three halides are determined in one aliquot. A determination takes 12-15 minutes. The method is simple and accurate.

2. The optimum initial concentration of H_2SO_4 for separate titration of I^- and Br^- with potassium iodate, and of Cl^- by the Volhard method, has been established.

3. The lowest initial concentrations of the halides which can be determined in their mixtures by titration have been found to be: for I^- 0.0014 N, Br^- 0.0180 N, and Cl^- 0.00170 N.

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METHODS FOR THE ISOTOPIC ANALYSIS OF WATER

4. A METHOD FOR THE COMPLETE ISOTOPIC ANALYSIS OF WATER

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In the present article a description is given of a method for complete isotopic analysis of water at deuterium concentrations ranging from 0 to 100 atomic % and of the heavy isotopes of oxygen for concentrations ranging from 0 to 3.5 atomic %, based on normalization of the isotopic composition of the oxygen in water *. This principle was used a long time ago for determination of low concentrations of D and O^{18} by Jones and Hall [1], and by Brodsky and coworkers [2]. Platinum was the catalyst used.

Morita and Titani [3] have shown that the reaction of isotopic exchange between gaseous oxygen and water oxygen proceeds readily on manganese oxide. This reaction has been studied in detail in the work of Karpacheva and Rozen [4] and in the work of many others [5-6]. We used it as the basis for developing the method described below. Measurements of the density of water before and after normalization were carried out by means of a variant of the drop method [7], in which use was made of liquids and operational techniques which enabled us to carry out reliable measurements on water containing any concentration of deuterium [8].

Oxygen was passed from a cylinder into the setup at the rate of 3 liter/ minute; it was dried by passing through a column filled with SiO_2 or Al_2O_3. At high D concentrations in the water, the oxygen was given a supplementary drying by passing it through two spiral traps cooled in liquid air. Nevertheless, as a result of the rapid throughput of O_2, such drying proved insufficient during analysis of samples with concentrations of D approaching 100 %. Accordingly, the O_2 was, in addition, passed through a bubbler filled with broken glass moistened with 2-3 ml of test sample, and through a trap immersed in a mixture of ice and salt, and finally was passed through a side tube into a 10-12 ml flask containing 2-5 ml sample (the maximum amount of water was taken when concentrations of D and O^{18} were high). The flask was connected to a tube ($d = 18$ - 20 mm, $l = 100$ cm) filled with catalyst (50 g) and fitted in an electric oven provided with a thermocouple. The temperature could be varied within the limits 450-800°. A small electric hot plate was used for heating flask plus test water. The water was evaporated at the rate of 1 ml/8 minutes. From the oven the mixture of water vapor and oxygen passed into a spherical condenser about 0.5 meter long; the latter was provided with a siphon through which tap water was circulated, and by means of which it could be lowered during drying of the apparatus. In order to decrease the carry over of test sample by oxygen, the receiver which was connected to the condenser was cooled with ice or a mixture of ice and salt. A rheometer was fitted at the end of the apparatus. Flasks and condenser were made of quartz and were connected by normal ground joints. When the O^{18} concentration in the water did not exceed 1.5 atomic %, the tube containing catalyst could be halved in size.

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* The mixture of heavy oxygen isotopes is arbitrarily denoted by O^{18} in the article. It is assumed, to a first approximation, that the densities of D_2O^{16} and H_2O^{18} are equal. The difference in densities of H_2O^{18} and H_2O^{17} is not taken into account.

The catalyst – manganese oxide – was prepared by precipitation of the hydrated oxide of manganese by ammonia from a solution of $Mn(NO_3)_2$. The filtered off $Mn(OH)_2$ was dried at 100° until a dough-like material was obtained; by passing this material through a sodium press, "small sausages" were prepared. After supplementary drying at 120°, the catalyst was loaded into the tube and heated at 450° in a stream of oxygen for 4-6 hours. Finally, vapors of distilled water were passed through the tube plus catalyst, until measurement of density confirmed the purity of the condensate.

On changing over from analyzing water with one concentration of heavy oxygen isotopes to another, it is recommended that water vapor with an isotopic composition approaching that of test sample be passed through the whole setup.

During analysis of water with high deuterium concentrations, in view of its hygroscopicity, it is necessary to pay particular attention to drying all the setup thoroughly, inclusive of traps and rubber connections. Dry oxygen was passed through the oven heated to 750° for 30-40 minutes. After the first normalization, this operation was carried out for 15 minutes. During work with heavy water it is essential that the latter should be in contact with the atmosphere for the minimum possible time. It is recommended that the oxygen cylinder used should have a pressure of not less than 50 atmospheres,since the moisture content of the gas increases with decreasing pressure.

In deciding on the conditions to be used for normalizing the isotopic composition of oxygen, we tried to ensure complete normalization in as short a time as possible and with the minimum number of operations. Consequently, it was necessary to use a high oxygen throughput and a high temperature. This has the disadvantage that it complicates drying of the oxygen, and lowers percentage condensation of test sample after normalization.

Even when we used a powerful column plus drier and two traps immersed in liquid air, for a one stage contact between water vapors containing 99.8 atomic % D (and not more than 0.06 atomic % O^{18}), the concentration of heavy isotopes was depressed by more than 0.2 atomic %. Consequently, the bubbler mentioned above was introduced in addition; in this bubbler traces of normal water remaining in the oxygen were held back by the heavy water.

Numerous and independent checks showed that this simple expedient was capable of limiting the dilution of test sample to only 0.02-0.06 atomic % at concentrations of 99-100 atomic % D. The error is greater the higher the D concentration. From changes in the D concentration of the heavy water in the bubbler during fixing of the throughput of gas, it was possible to judge the efficiency of various drying agents.

On the basis of a large amount of test data it is also possible to affirm that for the indicated O_2 throughput and rate of evaporation of test sample, complete normalization of the isotopic composition of oxygen for O^{18} contents up to 3.5 atomic % is achieved after two contacts in an oven 1 meter long at a temperature of 750° *. When the O^{18} content was lower than 1.5 atomic %, one contact was enough even for an oven 0.5 meter long and a temperature of 550°.

It is probable that during the exchange reaction, not only atmospheric oxygen, but oxygen from the catalyst participates. This was evident from the fact that when one took 30 g of catalyst (packed into a tube 40 cm long), it was possible at 700° to normalize completely 8 ml of water containing 0.5 atomic % O^{18}. Partial exchange occurred even after distillation of 30 ml of water in the absence of gaseous oxygen. When, after such a test, normal water was passed through the manganese oxide, it became heavier.

At an oven temperature of 550°, without additional cooling of the receiver, the loss of the sample amounted to 50% on an original sample of 3 ml, When the reciver was cooled to -10°,the loss dropped to 30%. For an oven temperature of 750° and a sample volume of 5 ml, with the receiver cooled in ice during distillation, 20% of test sample was lost; without cooling of the receiver the loss was 50%. In part the loss is the result of wetting of the apparatus and in part by carry over of water vapor by oxygen. In order to determine the error which is caused by separation of isotopes as a consequence of carry over of the vapors, experiments were carried out with water containing about 50% D, i.e. with a concentration at which the error has a maximum value. For a total loss of water of up to 30% of the amount taken (3 ml), the D concentration of the condensate

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* When the sample was heavily contaminated by organic materials and it was only important to know the D content of test sample, the water vapors were passed through a separate oven packed with manganese oxide; even at O^{18} concentrations up to 3.5 atomic % only one additional contact was found necessary.

increased by approximately 0.2 atomic %. This change in concentration corresponded to a carry over of 15% water, if one arbitrarily assumes that the D concentration changed as a result of relay distillation. At D concentrations in the distilled test water ranging from 0 to 10 and from 90 to 100 atomic %, the concentration changes by 0.01 atomic %. Such an error can be neglected. During analysis of water with another content, attention should be given to decreasing the carry over of water by improving cooling of the receiver, and, where necessary, to introducing corrections for fractionation of the isotopes [9].

Results for Complete Isotopic Analysis of Water Samples

Experiment No.	Before normalization $D+O^{18}$	First distillation		Second distillation		Third distillation	
		D	O^{18}	D	O^{18}	D	O^{18}
1	0.22	0.12	0.10	0.12	0.10		
2*	0.24	0.14	0.10				
3	1.28	0.84	0.44				
4*	1.32	0.82	0.50				
5	1.94	0.64	1.32	0.64	1.32		
6*	1.96	0.65	1.32				
7**	10.28	9.01	1.27	9.01	1.27		
8**	10.28	9.04	1.24	9.01	1.27		
9	10.31	7.22	3.09	7.22	3.11		
10	10.31	7.22	3.09				
11	15.43	12.00	3.43	11.99	3.44		
12	15.43	12.00	3.43	11.95	3.48		
13		98.18		98.12		98.12	
14		98.20		98.17			
15	99.92	99.83	0.09	99.76	0.16		
16	99.92	99.82	0.10	99.75	0.17		
17	99.93	99.87	0.06	99.82	0.11		
18	99.94	99.87	0.07	99.81	0.13		
19	97.84	96.52	1.54				
20*	97.84	96.52	1.54				
21	101.07	99.72	1.35	99.69	1.38		
22	101.08	99.69	1.39	99.70	1.38		
23	101.12	99.71	1.41	99.66	1.46		
24	101.14	99.73	1.41	99.71	1.43		
25	101.44	99.69	2.85	98.56	2.88		
26	101.42	98.58	2.84	98.52	2.90		
27	101.91	99.04	2.87	98.87	3.04	98.89	3.02
28	101.90	99.02	2.88	98.85	3.05	98.83	3.07
29	101.90	99.00	2.90	98.90	3.00	98.85	3.05

* Duplicates carried out by another operator.

** Experiments carried out by a third operator.

Using the method described for complete isotopic analysis of water, 2 ml of water is required at low concentrations of D and O^{18}, and up to 8 ml for high contents of D and O^{18}. The time taken to carry out an analysis varies from 1.5 to 2.5 hours according to volume of test sample and number of distillations.

Results of such measurements are given in the Table. Experiments Nos. 1-10 and Nos. 19-20 were carried out at 550° using a contact tube 0.5 meter long. The remainder were carried out at 750° in a contact tube 1 meter long.

Part of the sample was passed through the catalyst several times, while the receiver and condensate were connected to the front part of the tube.

Experimental accuracy is limited by the accuracy of density measurements by the drop method.

We wish to thank R.I. Grigoryeva and K.P. Voloshenko who carried out a series of control analyses.

SUMMARY

1. A semimicro method is described for complete isotopic analysis of water containing from 0 to 100 atomic % deuterium and from 0 to 3.5 atomic % heavy oxygen isotopes; it is applicable, in principle, to even greater contents of heavy oxygen isotopes.

2. Analysis is conducted with very simple apparatus and reagents; an analysis does not take long (1.5 - 2.5 hours), and the amount of test sample is small (2-8 ml of water, depending on concentration of heavy isotopes).

3. An analysis consists of measuring the density of water by the drop method, before and after normalization of the isotopic composition of oxygen in it, by bringing a mixture of water vapor and atmospheric oxygen into contact over manganese oxide at temperatures from 500-750°, depending on the concentration of heavy oxygen isotopes.

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* Original Russian pagination. See C. B. translation.

A POTENTIOMETRIC METHOD OF DETERMINING 3-NITROTOLUENE IN 2-NITROTOLUENE

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The most widely used method for the quantitative determination of the meta-isomer in most disubstituted benzenes having NH_2, OH, and NO_2 groups, is bromometric titration [1-3]. The method is based on the fact that the ortho-and para-isomers form dibromosubstituted derivatives with bromine, while the metal isomers give tribromosubstituted benzenes. The most widely used brominating agent is a bromide-bromate mixture, acidification of which leads to liberation of free bromine:

$$BrO_3^- + 6H^+ + 5Br^- = 3Br_2 + 3H_2O$$

The bromometric method is generally used at present for analyzing isomeric toluidines and nitrotoluenes [4]. In the latter case, the nitrotoluenes are reduced beforehand to the corresponding toluidines. Determination is carried out by parallel bromination and diazotization on aliquots of test material. Titration end point is established by tests with starch-iodide paper. When the content of metal-isomer is low (1-3%), the method gives very low results. The main difficulty is determination of the titration end point. The use of starch-iodide paper as an indicator for the end point introduces a number of errors. Another source of error is the low reaction rates of bromination and diazotization, particularly near the equivalence point.

It was suggested as long ago as 1925 that control of diazotization could be achieved by a potentiometric method [5]. Subsequently, this method was used for determining a large number of amines [6-11].

It has also been demonstrated that diazometric determination can be successfully carried out by "slowing down the end point" [12-13]. The principle of this method is based on the depolarizing effect of nitrous acid on the indicator circuit consisting of two platinum electrodes lowered into the solution being titrated. A small potential difference is applied from an outside emf source to the electrodes. A sensitive galvanometer included in the circuit shows a sharp increase in current at the point where excess nitrous acid becomes available in the solution.

Other suggestions have been made for determining the end point in different types of bromometric titrations, including titration of amines; these include amperometric determinations of the end point [14-15], the method of "slowing down the end point" [16-18], spectrophotometric [19], and potentiometric [20-22] methods.

The aim of the work described here was to develop a potentiometric method of determining 3-nitroluene in 2-nitroluene when the content of the former is low (1-3%).

EXPERIMENTAL

Apparatus

A P-4 potentiometer manufactured by the Moskip factory was used for measuring e.m.f. during titration. The galvanometer sensitivity was 0.6 μ amperes/division. A saturated calomel half-element was used as reference electrode. The indicator electrode was a platinum plate fused into a glass tube.

Starting Materials and Reagents

These include: sodium nitrite, a 0.2 N solution. The standard nitrite solution was prepared from technical grade $NaNO_2$ (about 14.4 g/ liter of solution). The exact normality was established potentiometrically using sulfanilic acid.

Potassium bromate -- 0.4 N solution. Standard bromate solution was prepared by dissolving the exact amount of chemically pure grade $KBrO_3$ in water; the $KBrO_3$ was dried to constant weight beforehand. The normality was calculated.

Sulfanilic acid (chemically pure grade) was dried at 120° to constant weight.

2-Nitrotoluene was purified by fractional distillation under vacuum. The setting point was -8.9°.

3-Nitrotoluene was purified by freezing out and subsequent distillation. The setting point was +15.5°

Procedure

Reduction of the Nitrotoluenes. About 6 g of the nitrotoluenes weighed to an accuracy of 0.01 g was washed with 20% H_2SO_4 (125 ml) in a 500 ml conical flask fitted with a ground glass stopper. A long glass tube which served as a reflux condenser was connected to the flask. 25 g of zinc dust was then added in two lots. The flask was shaken thoroughly for 2-3 minutes until the solution was decolorized. The tube was washed with hot distilled water and the flask connected to a reflux condenser fitted with a water sleeve; the solution was boiled for 10 minutes. The hot solution was filtered on a suction funnel and on cooling was transferred to a 500 ml standard flask. Aliquots for bromination and diazotization were taken at the same time in two separate beakers.

Diazotization. 100 ml of the solution of reduced nitrotoluenes was transferred to the titration beaker, and 15 ml of dilute HCl 1:1 and 100 ml of 10% KBr solution added. Titration was carried out at 22-25°. The tip of the buret was immersed in the liquid being titrated. Towards the end point, the buret was raised a little above the solution, and nitrite added two drops at a time, an interval of 3 minutes being allowed to elapse between each addition (approximately 0.07 ml). The end point was established on the basis of the maximum increase in potential.

Bromination. 50 ml of test solution was transferred to the titration vessel; 15 ml of dilute HCl 1:1 and 150 ml of 10% KBr were then added. The solution being titrated had a temperature of 22-25°. Titration was carried out the same as for diazotization.

If the content of 2-nitrotoluene in the test material be denoted by x, while the 3-nitrotoluene content is denoted by (100 - x), then

$$100 - x = 200\left(\frac{K \cdot a}{K_1 \cdot 6} - 1\right)\%,$$

where K is the correction coefficient for the normality of the bromate; K_1 is the correction coefficient for normality of nitrite; and a is the amount of bromate used in mls for 50 ml of test solution; b is the amount of nitrite used in mls.

RESULTS AND DISCUSSION

For the quantitative determination of nitro compounds in technical products a very convenient method is used, according to which the nitro compound is first dissolved in glacial acetic acid, it is then reduced and diazotized in hydrochloric and acetic acid media. Our experiments showed that the presence of acetic acid in solution sharply depressed the sensitivity of potentiometric titration (diagram).

Reduction of nitroluenes in hydrochloric acid in the absence of acetic acid proceeds rapidly and quantitatively; nevertheless, according to our preliminary tests, the results of bromometric titration are low in this case.

In our experiments we varied the temperature of titration from 0 to 60°. Titration at low temperatures led to poorer results. The potential was established very slowly and there was no clear cut potential jump at the end point. By increasing the temperature to about 30°, the analysis could be speeded up and the end point defined more clearly. Increasing the temperature further led to poorer reproducibility.

The KBr concentration in the solution being titrated was varied within the limits of 0.1-0.5 N. The latter concentration proved to be the best. Increasing the KBr concentration further had no effect on the accuracy of titration.

Changing the HCl concentration in the solution being titrated, up to certain limits, had no effect on titration accuracy.

TABLE

Potentiometric Titration of Nitrotoluenes

Product	Weight taken, in g	3-Nitrotoluen content of sample, in %	Found in %	Error	
				Absolute, in %	Relative, in %
3-Nitrotoluene	3.93		96.5		
	3.90		96.8		
2-Nitrotoluene	5.77	0.0	0.0	±0.0	
	5.42	0.0	0.1	+0.1	
	5.40	0.0	0.1	+0.1	
99% 2-Nitrotoluene + 1% 3-Nitrotoluene	5.40	0.967	0.9	−0.07	7.2
	5.40	0.967	0.9	−0.07	7.2
	5.40	0.967	0.8	−0.17	17.5
97% 2-Nitrotoluene + 3% 3-Nitrotoluene	5.70	2.90	2.8	−0.1	3.5
	5.80	2.90	2.9	±0.0	0.0
	5.57	2.90	3.2	+0.3	10.3
	5.54	2.90	2.9	±0.0	0.0
	5.57	2.90	2.9	±0.0	0.0
95% 2-Nitrotoluene + 5% 3-Nitrotoluene	5.40	4.84	4.9	+0.06	1.2
	5.40	4.84	5.0	+0.16	3.2
	5.40	4.84	4.6	−0.24	4.8

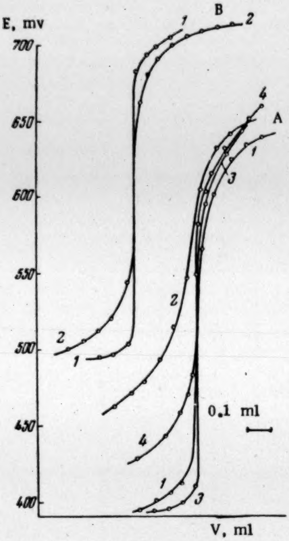
Near the equivalence point there was observed a potential jump at the moment of addition of portions of nitrite or bromate. Until the equivalence point had been reached, the potential, after an initial jump, decreased again, testifying that titration was not yet complete. On addition of the first potion of nitrite or bromate in excess, the potential remained practically constant or slowly increased (this was characteristic of diazotization). In this connection, therefore, determination of the end point could be simplified by titrating to a constant potential in the course of 30-60 seconds.

On the diagram are shown titration curves obtained by taking the potential readings 3 minutes after addition in turn of portions of nitrite or bromate. These values did not correspond to equilibrium values (the potential continued to change slowly); nevertheless, as the diagram shows, they characterize quite clearly the path of the titration.

Control experiments with freshly prepared starch-iodide paper showed that bluing is observed 2-3 drops after the end point determined potentiometrically.

The table contains results of potentiometric analysis of original nitrotoluenes and synthetic mixtures.

The method described for determining 3-nitrotoluene in 2-nitrotoluene has been checked and accepted into practice for production determination in the Rubezhansk Chemical Combine.



Curves for bromometric and diazometric titration:
A) Titration with 0.2 N $NaNO_2$; 1) 2-nitrotoluene reduced in 20% H_2SO_4 (125 ml); 2) 2-nitrotoluene reduced in a mixture of 50 ml glacial acetic acid + 125 ml 20% H_2SO_4; 3) annealed platinum electrode; 4) an electrode which had been used for three days (2-nitrotoluene reduced in 20% H_2SO_4).
B) Titration with 0.4 N KBr. 1) annealed platinum electrode; 2) electrode which had been used for three days.

SUMMARY

A method has been developed for the potentiometric determination of 3-nitrotoluene in 2-nitrotoluene. The maximum experimental error is ± 0.3%.

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A REFRACTOMETRIC METHOD FOR CONTROLLING PRODUCTION OF INTERMEDIATES AND DYES

PART I. DETERMINATION OF PARA-NITROCHLOROBENZENE IN ORTHO-NITROCHLOROBENZENE

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A solution of the problem of a separate determination of p-nitrochlorobenzene I, in o-nitrochlorobenzene, II, during distillation of mononitrochlorobenzene, helps to solve the problem of automatic control of distillation and crystallization during the production of the products indicated. Published data relating to the refractive index and specific gravity of the products we are interested in, and of their mixtures, is limited, and is not sufficiently reproducible. The following problems confronted us:

1. To study melting point diagrams of I and II.

2. To determine the specific gravity of mixtures of I and II in the range 30-90°.

3. To study the refractive index isotherms of systems I and II for 40, 50 and 70°.

4. Determination of the temperature coefficient for the refractive index, and determination of the polytherms for the pure components.

A. Original Materials

1. Reagent grade o-nitrochlorobenzene; setting point +31.8°

2. Reagent grade p-nitrochlorobenzene; setting point + 82.5°

3. The original mixtures were prepared from these materials by mixing exact amounts of the components; they were controlled by reference to setting temperatures according to the diagram (Fig. 1).

B. Procedure

1. Setting temperature was determined in a Zhukov apparatus. The accuracy of temperature measurements was ± 0.2°.

2. Specific gravity was determined by means of 50 and 25 ml pyknometers; their exact volume was determined with water at 20and 50°. All iso- and polythermal studies were carried out at constant temperature (± 0.2°). Materials were kept at a given temperature for 30 minutes before measurement.

3. Refractive index was determined on an Abbe refractometer. The accuracy with which measurements were made was ± 0.0002. Thermostating was carried out with an accuracy of ± 0.2°. On changing the temperature, 30 minutes were allowed to elapse before the next measurement. Three determinations of the refractive index were made on two samples of each mixture or pure component.

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* M.A. Pochvimaya did some of the experimental work.

C. Experimental Results

Results of determination of setting points of mixtures of I and II are given in Table 1 and Fig. 1.

The polytherms for the refractive index are shown in Fig. 2, while the calculated values for the temperature coefficients are given in Table 2.

TABLE 1

Determination of Setting Temperature (ST) of Mixtures of Ortho- and Para-nitrochlorobenzenes

ortho, in %	para, in %	Setting temperature, °C
100	0	+32.05
95	5	+29.10
90	10	+26.40
50	50	+38.40
33	67	+55.80
10	90	+75.20
5	95	+78.80
0	100	+82.75

TABLE 2

Values for the Temperature Coefficients of the Refractive Index for Ortho-nitrochlorobenzene and Para-nitrochlorobenzene and their Mixtures

ortho, in %	para, in %	dn/dT
100	0	0.00050
90	10	0.00050
50	50	0.00050
33	67	0.00050
10	90	0.00050
0	100	0.00040

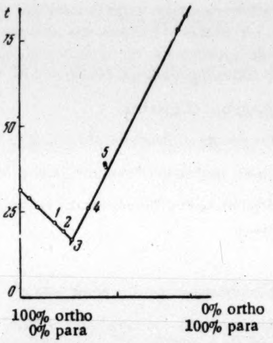

Fig. 1. Setting temperature of o- and p-nitrochlorobenzene systems

The polytherm for specific gravity is given in Fig. 3. The refractive index isotherms at 70, 50, and 40° for ortho and para nitrochlorobenzenes are given in Fig. 4.

From the results obtained, it follows that at constant temperature, a change in content of para in ortho-nitrochlorobenzene of 1% corresponds to a change of 0.00018 in the refractive index.

The refractometric method which we have developed has been checked during control of distillation operations of ortho-nitrochlorobenzene.

The results obtained were compared with those obtained using the setting temperature. The reproducibility (Table 3) is evident from Fig. 5.

Technical progress in apparatus construction has made it possible to construct a refractometer with a higher sensitivity than the Abbe instrument. Consequently it should be possible to lower the experimental error considerably as compared with our error of ± 1%; this should be valuable for controlling final distillation stages.

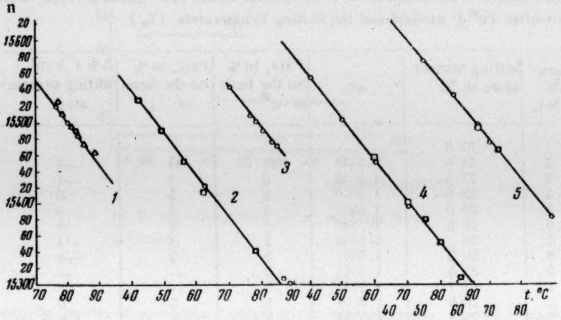

Fig. 2. Polytherms of the refractive index for mixtures of o-and p-nitrochlorobenzene systems

1) para-nitrochlorobenzene- $\frac{dn}{dT}$ = 0.0004;

2) ortho-nitrochlorobenzene- $\frac{dn}{dT}$ = 0.0005;

3) mixtures: 10% ortho; 90% para; $\frac{dn}{dT}$ = 0.0005;

4) mixture: 90% ortho; 10% para; $\frac{dn}{dT}$ = 0.0005;

5) mixture: 50% ortho- and 50% para; $\frac{dn}{dT}$ = 0.0005.

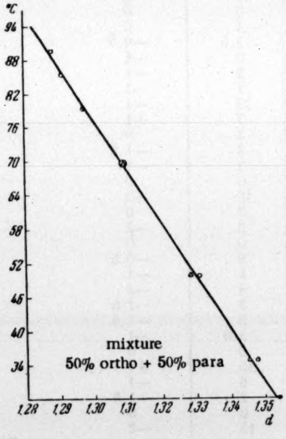

Fig. 3. Specific gravity polytherms.
O) mixture; △) ortho-isomer; □) para-isomer

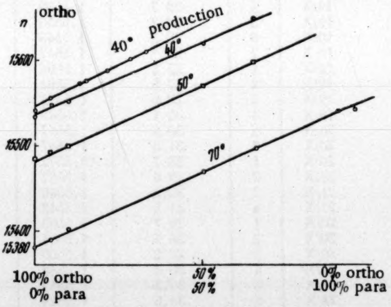

Fig. 4. Refractive index isotherms for ortho-para nitrochlorobenzene systems

TABLE 3

Comparison of Results of Determinations of Percentage Ortho and Para-nitrochlorobenzenes by the Refractometric (n^{40}) Method and the Setting Temperature (T_s)

Date •	Sample No.	Setting temperature in °C	n^{40}	Para, in % on the basis of n^{40}	Para, in % on the basis of T_s	Δ% ± k of setting temperature
16/X	1	27.6				
17/X	2	24.6	1.5573	13	14	—1
17/X	3	27.9	1.5558	6	7	—1
17/X	4	28.6	1.5556	5	5	0
17/X	5	28.9	1.5555	5	5	0
17/X	6	29.6	1.5549	2	3	—1
17/X	7	30	1.5550	2	3	—1
17/X	8	30.3	1.5547	1	2	—1
17/X	9	31.5	1.5545	0	—	—
17/X	1	12.7	1.5612	33	—	—
17/X	2	28.5	1.5556	5	5	0
17/X	3	29.1	1.5553	3.5	4	—0.5
18/X	4	30.3	1.5547	1	2	—1
18/X	5	30.5	1.5547	1	2	—1
18/X	6	31.5	1.5548	1	0	+1
17/X	1	12.4	1.5614	34	—	—
18/X	2	29 6	1.5552	3	3	0
18/X	3	30.1	1.5549	1.5	2	—0.5
18/X	4	31.5	1.5546	0	—	0
17/X	1	21.9	1.5588	21	—	—
19/X	2	25.8	1.5572	12.5	12	+0.5
19/X	3	29.7	1.5552	3	4	—1
19/X	4	30.5	1.5550	2	2	0
19/X	5	31.5	1.5546	0	0	0
18/X	1	24.2	1.5576	15	15	0
19/X	2	25 9	1.5569	12	11.5	+0.5
19/X	3	27.9	1.5560	7	7	0
19/X	4	29.1	1.5557	5	5	0
19/X	5	30.2	1.5548	1	2	—1
20/X	6	30.7	1.5549	1.5	1.5	0
20/X	7	31.5	1.5545	0	0	0
18/X	1	24.2	1.5576	15	15	0
19/X	2	28.9	1.5557	5	5	0
19/X	3	29.4	1.5554	4	4	0
19/X	4	29.7	1.5550	2	2.5	—0.5
19/X	5	30.2	1.5550	2	3	—1
19/X	6	30.3	1.5548	1	2	—1
19/X	7	30.7	1.5547	0	1	—1
19/X	1	25.3	1.5568	11	12	—1
19/X	2	27.5	1.5562	8	7	+1
19/X	3	28.9	1.5555	5	5	0
19/X	4	30.1	1.5549	1.5	3	—1.5
20/X	5	30.5	1.5547	1	2	—1
20/X	6	31.5	1.5547	0	0	0
20/X	1	23.7	1.5572	13	15	—2
21/X	2	29.6	1.5552	3	3	0
21/X	3	30.5	1.5546	0	2	—2
21/X	4	31.5	1.5543	0	0	0
20/X	1	26.7	1.5563	8.5	9	—0.5
20/X	2	28.5	1.5554	4	5	—1
20/X	3	29.2	1.5550	2	4	—2
21/X	4	30.2	1.5548	1.5	3	—1.5
21/X	5	30.3	1.5549	1.5	3	—1.5
21/X	6	30.5	1.5548	1.0	2.0	—1
21/X	7	31.5	1.5543	0	0	0
20/X	1	24	1.5579	16	15	+1
20/X	2	28.1	1.5556	5	6	—1
20/X	3	30.4	1.5547	0.5	2	—1.5
20/X	4	31.5	1.5543	0	0	0
20/X	1	24.1	1.5572	13	15	—2
21/X	2	28.5	1.5558	6	5	+1
21/X	3	30 6	1.5547	0.5	2	—1.5
21/X	4	31.6	1.5542	0	0	—

• 16/ X = Oct. 16, etc. – Publisher's note.

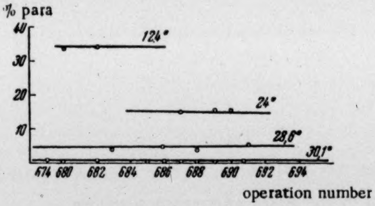

Fig. 5. Reproducibility of "n" readings from operations

SUMMARY

1. The specific gravity of pure ortho- and para-nitrochlorobenzene, and their mixtures, has been determined at 30-90°. The temperature coefficient of the specific gravity was found to be 0.001; this is in agreement with published results for these materials.

2. Polytherms have been constructed for the refractive index or pure ortho- and para-nitrochlorobenzene, respectively and their mixtures, in the range 40 to 90°. The temperature coefficient of the refractive index is 0.0005.

3. Isotherms have been constructed for 70, 50, and 40°, and it has been shown that changes in the value of the refractive index for mixtures of the ortho and para isomers are additive.

4. It has been shown that a change of 1% in the content of the para in the ortho isomer leads to a change of 0.00018 in refractive index.

The reproducibility of analyses carried out on a single test material, and on samples taken from different operations but having the same setting temperature, is ± 1% of para-nitrochlorobenzene. This is better than the reproducibility of ± 2% required for technical control.

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QUANTITATIVE DETERMINATION OF ALCOHOLS BY THE DEHYDRATION METHOD

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The literature relating to the use of dehydration for quantitative determination of alcohols is scant. Ikeda and Takeda [1] in 1936 were the first to suggest a method for the determination of linalool, terpineol, and also cineole, which was based on dehydration of these compounds in xylene solution over zinc chloride, and measurement of the volume of water evolved in a Dean and Stark apparatus. Bogatyrev, Dridze, and Rozhnov [2], quite indepenantly of the authors mentioned, also used dehydration with subsequent measurement of the water formed, for analyzing castor oil. The dehydration method has been used in the USSR for determining linalool in coriander oil. Guenther and Langeneau [3] have recommended dehydration of linalool over iodine for determination of the former. Quantitative release of water at the temperature of boiling toluene can be achieved in the case of all tertiary alcohols, when the following catalysts are used: sulfuric acid, potassium bisulfate, zinc chloride, and iodine [4].

Particularly rapid dehydration is observed when activated clay – askanite – and toluenesulfonic acid are used [5].

In the form proposed by the Japanese research workers, the method has a number of disadvantages, such as: the necessity of using large samples; the inaccuracy of measuring the volume of water evolved; and the difficulty of achieving complete removal of water in apparatus operating with a reflux flow of solvent. These disadvantages led us to search for improved methods of carrying out the dehydration reaction during determination of tertiary alcohols.

The possibility of using small amounts of test material during dehydration has been demonstrated by Polyakov and Turetyeva [6]. These authors determined linalool by dehydrating small samples in a sealed ampoule in the presence of sulfuric acid, and measuring the water given off by volume.

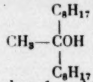
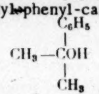
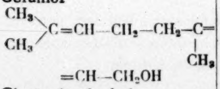
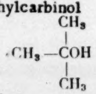
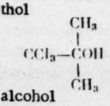
In our opinion the most accurate method of measuring the water given off is the Karl Fischer titration method. Accordingly we concentrated our attention on establishing conditions which would be suitable for carrying out titration. The solutions used for the Karl Fischer titration have a very low titer. The weight of test alcohol should be such that the amount of water given off does not exceed 40-50 mg. But, under such conditions, the loss of 1 mg of water leads to an error of 2%. It was essential therefore to find conditions which would guarantee freedom from any possibility of loss of water.

Attempts to dehydrate alcohols, mainly linalool, at room temperature proved unsuccessful. Somewhat better results were obtained on heating to temperatures below 100°. Thus, linalool, in a methanol medium in the presence of sulfuric acid, was completely dehydrated, but the repeatability and accuracy of the determination were not good enough.

Good results were obtained for linalool and some other alcohols in acetic acid media, in the presence of insignificant amounts of sulfuric acid [7]. On heating linalool to 50° in closed flasks in a solution of acetic acid, the amount of water given off was equivalent to the amount of alcohol taken. The water was measured by the Karl Fischer method. True, under such conditions, two reactions – dehydration and acetylation – occur;

both, as our experiments showed, to roughly the same extent; all the same, as the result of one reaction or the other, one molecule of water is evolved per molecule of alcohol.

TABLE 1
Determination of Alcohols by the Dehydration Method

Alcohol	Sample weight in g	Amount of water, in g	Alcohol found, in %	Notes
Linalool No. 1	0.6160	0.070	87.2	Extracted from Salvia sclarea; found by Method No. 1 97.0%
	0.5039	0.0574	87.4	
Linalool No. 2	0.4313	0.0474	84.0	Extracted from Coriander oil; found by Method No. 1 94%.
	0.4842	0.0531	93.6	
Coriander Oil № 1			64.6	Found by Method No. 1 64.9% linalool
№ 2			66.2	64.2%
№ 3			69.2	69.4%
№ 4			73.7	74.3%
Terpineol	0.3908	0.0453	99.1	n^{20} — 1.4830
	0.3852	0.0445	98.8	
Cedrol	0.4785	0.0387	99.7	Crystalline, m.p. 83.5°
	0.4702	0.0379	99.6	
Sklareol	0.5017	0.0564	96.2	Crystalline
	0.4905	0.0552	96.4	
Dioctyl-methyl-phenyl-carbinol	0.4427	0.0214	95.1	
 $CH_3-\overset{C_8H_{17}}{\underset{C_8H_{17}}{COH}}$	0.5252	0.0255	95.3	
Methyl-phenyl-carbinol $CH_3-CHOH-C_6H_5$	0.4167	0.0595	99.2	
Dimethyl-phenyl-carbinol  $CH_3-\overset{C_6H_5}{\underset{CH_3}{COH}}$	0.4528	0.0594	99.0	Crystalline
4-Hydroxy-3-methoxyphenyl $(CH_3O)(OH)C_6H_4-CHOH-C_2H_5$	0.4160	0.0407	99.0	Crystalline, m.p. 82°
Geraniol	0.4411	0.0474	91.98	Alcohol determined by acetylation 95.5%; citronellol may be present
 $\begin{matrix}CH_3\\CH_3\end{matrix}>C=CH-CH_2-CH_2-\underset{CH_3}{C}=CH-CH_2OH$	0.3665	0.0389	91.0	
Cinnamic alcohol	0.4765	0.0309	48.4	Determined by acetylation 96.%
Trimethylcarbinol  $CH_3-\overset{CH_3}{\underset{CH_3}{COH}}$	0.4667	0.0114	10.0	Heated for 5 minutes
Chlorethol  $CCl_3-\overset{CH_3}{\underset{CH_3}{COH}}$	Not dehydrated			
Decyl alcohol	»	»	»	
Citronellol	»	»	»	
Isobutyl alcohol	»	»	»	
Benzyl alcohol	»	»	»	
Phenyl ethyl alcohol	»	»	»	
Menthol	»	»	»	
Borneol	»	»	»	

The method which we have developed, and which we shall call Method No.1, is similar to the method used by Bryant, Mitchell, and Smith [8]; in the latter method the alcohols are esterified with acetic acid in the presence of boron fluoride, and the amount of alcohol is determined on the basis of the amount of water evolved during esterification. Under the conditions we employed, esterification in the presence of sulfuric acid occurs at a lower temperature and there is no need to use boron fluoride.

Nevertheless, the method of dehydrating in acetic acid does not permit separate determination of tertiary alcohols in the presence of primary and secondary alcohols, since, under the reaction conditions used, the latter are esterified. Furthermore, the success of a determination depends on the quality of the acetic acid and its content of water and acetic anhydride.

We found that acetic acid of high concentration may contain some acetic anhydride as well as small amounts of water; the fact that the anhydride may be present is reflected in the results. We succeeded in solving the problem of carrying out a rapid and accurate determination of tertiary alcohols in the presence of secondary and primary alcohols by carrying out dehydration in the presence of toluenesulfonic acid.

Dehydration in a medium of boiling toluene in the presence of toluenesulfonic acid goes to completion so rapidly in the case of linalool and other tertiary alcohols, that there is no risk of losing water. The reaction is carried out in an ordinary flask fitted with a reflux condenser; determination is finished off by titrating with the Karl Fischer reagent. The results obtained are given in Table 1.

As we have already pointed out, the capacity to split off water more readily is determined, not only by the tertiary position of the hydroxyl group, but also by the structure of the rest of the alcohol molecule.

TABLE 2

Optimum Conditions for Dehydration of Linalool

Amount		Heating time, in minutes	Linalool found, in %
Catalyst, as % of linalool	Toluene in ml		
1.5	10	5	15.6
2.5	10	5	56.1
3.5	5	5	84.6
4.5	10	5	90.2
5.0	5	5	91.2
10.0	10	5	91.7
12.5	10	5	91.7
14.2	10	5	90.8
20.0	10	5	92.3
11.0	5	10	91.2
10.5	10	10	92.0

Geraniol, methylphenylcarbinol, 4-hydroxy-3-methoxyphenylethyl-carbinol are dehydrated as well as the tertiary alcohols.

While a tertiary alcohol such as chlorethol is not dehydrated at all, trimethylcarbinol, although it is dehydrated, is dehydrated so slowly that partial loss of water results, and quantitative results can not be obtained. As the results given in Table 1 show, crystalline alcohols, which can be prepared in a pure form, give results which approximate to theory. For liquid alcohols, the criteria of purity used were the physical constants and the hydroxyl content as determined by some other method.

We should like to point out that dehydration proceeds rapidly enough in the presence of sulfuric acid also; this catalyst, however, leads to some side reactions, which led us to prefer and recommend toluenesulfonic acid as catalyst. Sulfuric acid can however, be used in some individual cases.

Establishment of optimum conditions for carrying out dehydration in the presence of toluenesulfonic acid was carried out using linalool as test material. The linalool used was extracted from coriander oil which contained 91.5% of the former. This value was checked by aquametric method No. 1 (dehydration in acetic acid). 8.485 g of linalool was dissolved in 100 ml toluene and 5 ml lots of this solution used for the series of determinations. Table 2 contains the results of a study of the effect of amount of catalyst, solvent, and time of heating. On the basis of these results it was found that the optimum conditions are as follows: sample weight about 0.5 g; 10 ml of solvent; and 5 minute heating in the presence of catalyst taken in an amount equal to 5-10% of the weight of test alcohol.

Experimental Procedure. 1-1.2 g of test alcohol is dissolved in a 25 ml flask in toluene. Into a 50 ml round bottom, long necked flask (8-10 cm long) connected via a ground glass joint with a small reflux condenser, was placed the weight of catalyst to be used (0.02 - 0.045 g); 10 ml of the prepared solution of test alcohol is then pipetted into this flask, and the mixture boiled for 5 minutes, taken from the beginning of boiling. A control test is put on at the same time, the same amount of solvent and catalyst being used. When reaction is complete and the flask is cold, the condenser is washed with 5 ml of dry methanol measured out with a pipet, and the flask disconnected from the condenser. The mixture is titrated with Karl Fischer reagent. The moisture content of the test alcohol is determined in a separate experiment.

SUMMARY

A method has been developed for the determination of tertiary alcohols, which is based on dehydration in the presence of toluenesulfonic acid as catalyst; the water given off is titrated with Karl Fischer reagent.

It has been demonstrated that the method is applicable to the determination of tertiary and readily dehydrated primary and secondary alcohols in the presence of stable (saturated) primary and secondary alcohols.

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IODOCHLOROMETRIC DETERMINATION OF BARBITURIC ACID DERIVATIVES

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The theoretical bases of the iodochlorometric method and numerous examples of its application have been described in the work of Gengrinovich, Kagan, and Fialkov [1]. Of the barbiturates used in medical practice, some of them, which contain the thiogroup $=CS$ (thiopental*) or a double bond in the cyclohexanyl radical (evipan** and phanodorn***), or in the aliphatic allyl group (malil****), are capable of reacting with a hydrochloric solution of iodine chloride.

The aim of the work described here was to develop the iodochlorometric method for quantitative determination of the preparations listed above.

Iodochlorometric Determination of Sodium Thiopental

Several methods have been published for the quantitative determination of materials containing the thiogroup; these include determination of sulfur by the Carius method, oxidation of sulfur to sulfate by means of KNO_3, $KMnO_4$, $KClO_3$, etc. More specific, in the present instance, are methods which involve oxidation of the sulfide sulfur of the thiogroup with iodine in alkaline media, followed by titration of excess iodine [2], or by the action of excess ammoniacal solution of silver nitrate and determination of the sulfur as silver sulfide [3].

In conjunction with Vaisman, it was suggested that an acidimetric method could be used for quantitative determination of sodium thiopental [4].

We have already shown [5] that on addition of a hydrochloric acid solution of iodine chloride to an aqueous solution of sodium thiopental, oxidation of the sulfur of the $=CS$-group occurs to give sulfuric acid, with simultaneous formation of 8 equivalents of hydrochloric acid and 8 equivalents of iodine. Under these thiopental is converted into ethyl-(methyl-butyl) barbituric acid (etaminal). The reaction proceeds as follows:

$$R(R_1)C(CO-NH)CS + 8ICl + 5H_2O = R(R_1)C(CO-NH)CO + H_2SO_4 + 8HCl + 4I_2.$$

In order to find the optimum conditions of carrying out this reaction, with a view to using it for developing a quantitative method of determining sodium thiopental, the following factors were studied: amount of reagent and water, temperature of the medium, and duration of reaction.

Since the sodium thiopental issued commerically contains 5-5.5% of sodium carbonate, we undertook to establish the necessary conditions for the reaction, using this preparation, as well as the acid form of thiopental which was prepared by extraction from an acid medium with ether, followed by drying at 70°. In order to get quantitative results, the temperature of the reaction medium should be about 70°, while for each 0.05 g of

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* Ethyl-(methyl-butyl)-thiobarbituric acid

** Methyl-cyclohexenyl-N-methyl-barbituric acid

*** Ethyl-cyclohexenyl-barbituric acid

**** Diallyl-barbituric acid

preparation it is necessary to add not less than 100-150 ml of water. The amount of thiopental was determined as follows:

1. From the amount of iodine liberated during reaction of barbiturate and a hydrochloric acid solution of iodine chloride. The liberated iodine was extracted with chloroform and titrated with 0.1 N sodium thiosulfate. The gram equivalent was shown to be M/8. 0.0336 and 0.0412 g of thiopental corresponded to 11.10 and 13.30 ml of 0.1 N $Na_2S_2O_3$, respectively. The theoretical values on the basis of the formula, $C_{11}H_{18}O_2N_2S$ were 11.10 and 13.61 ml of 0.1 N $Na_2S_2O_3$.

2. From the weight of combined iodine chloride, excess of the latter being decomposed (after extraction of liberated iodine) with potassium iodine, and the iodine liberated titrated with 0.1 N sodium thiosulfate ($ICl + KI = KCl + I_2$). The gram equivalent in this case was found to be M/16.

0.0336 and 0.0412 g of thiopental combined with the following amounts of ICl, in terms of 0.1 N Na_2SO_3: 22.00 and 26.90 respectively. The theoretical values on the basis of the formula $C_{11}H_{18}O_2N_2S$ were 22.20 and 27.22.

3. From the total iodine liberated during reaction of ICl with thiopental and during the reaction between excess ICl and potassium iodide. The gram equivalent in this case was found to be M/8.

0.0513 and 0.0434 g of thiopental corresponded to 16.74 and 14.16 ml of 1 N $Na_2S_2O_3$. The calculated values on the basis of the formula $C_{11}H_{18}O_2N_2S$ were 16.94 and 14.33.

On the basis of these results we have developed a method for quantitative determination of sodium thiopental in the presence of sodium carbonate, which consists of the following: a sample weight amounting to one ampoule (about 1 g of the preparation) is dissolved in water in a 100 ml standard flask and made up to the mark with water.

1) Titration of Total Sodium Thiopental and Sodium Carbonate: To 5 ml of the solution obtained is added 5 ml of chloroform and the whole titrated with 0.1 N hydrochloric acid using Methyl Orange as indicator.

2) Determination of Sodium Thiopental: to another 5 ml aliquot of the solution, contained in a 250 ml ground neck flask is added 150 ml of boiling water, and 20 ml of a 0.25 N hydrochloric acid solution of iodine chloride* rapidly added to this. After standing for an hour the liquid is cooled to room temperature, and 20 ml of 10% potassium iodide added; the liberated iodine is titrated with 0.1 N sodium thiosulfate. 1 ml of a 0.1 N hydrochloric acid solution of iodine chloride corresponds to 0.0033 g of sodium thiopental.

The amount of carbonate in the aliquot is calculated by means of the formula: $(a - b/8)\ 0.0053$, where a is the amount in mls of 0.1 N hydrochloric acid used for the total titration(carbonate+thiopental); b is the amount in mls of 0.1 N hydrochloric acid solution of iodine chloride used for titrating sodium thiopental.

Results obtained are given in Table 1.

TABLE 1

Determination of Sodium Thiopental in the Presence of Sodium Carbonate by Means of a Hydrochloric Acid Solution of Iodine Chloride

Sample weight	0.1 N ICl combined, in ml	Sodium thiopental			0.1 N HCl solution used, in ml	Sodium carbonate		
		Found		As specified in the Pharmacopeia		Found		As specified in the Pharmacopeia
		In g	In %	In %		In g	In %	In %
0.0490	14.04	0.0463	94.5	94.3	2.20	0.00236	4.8	4.7
0.0476	13.58	0.0448	94.1		2.10	0.00214	4.1	
0.0747	20.50	0.0677	94.4		3.20	0.00338	4.7	

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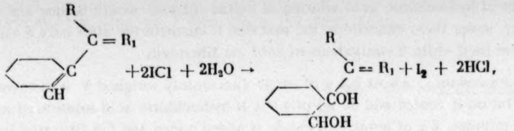
* In view of the liberation of iodine vapor it is necessary to add the ICl very quickly; it is advisable therefore to measure out the requisite amount of the hydrochloric acid solution of iodine chloride beforehand, in a separate beaker. The reagent is added from this beaker to the hot solution, while on cooling the solution, the beaker is washed with water and the washings added to the reaction mixture.

Iodochlorometric Determination of Barbiturates Containing the Cyclohexenyl Group: Phanodorn and Sodium Evipan

According to published results [6, 7], when bromine is allowed to react with preparations containing a cyclohexenyl group in their molecule (terpineol, barbiturates), the bromine adds on to the double bond to give a dibromo derivative; in those cases where the material contains still another double bond (terpinolene, limonene) the tetrabromo derivative is obtained.

On the basis of previous studies [8], we have advanced the view that the interaction between barbiturates containing the cyclohexenyl group and a hydrochloric acid solution of iodine chloride can be represented by the following equation:



where $R = C_2H_5$ or CH_3

$R_1 = \rangle(CO-NH)_2CO.$

The following factors were studied in order to estabiish the optimum conditions for quantitative determination of phanodorn and evipan: the amount of reagent, duration of interaction, and the effect of temperature.

Investigation was carried out in the same way as for thiopental. It was shown that it is necessary to take not less than $1^{1}/_{2}$ -2 times the theoretical amount of the hydrochloric acid solution of iodine chloride. The reaction with evipan is quantitative at the end of 30 minutes at room temperature; with phanodorn the reaction is only quantitative when a temperature of 50-60° is used.

On the basis of the results obtained, the following method can be put forward for the quantitative determination of phanodorn and sodium evipan.

Phanodorn. About 0.1 g of phanodorn (weighed accurately) is placed in a ground neck flask and dissolved on heating in 5 ml of 0.1 N sodium hydroxide; 25 ml of boiling water is then added, followed by 7.5 ml of a 0.25 N hydrochloric acid solution of iodine chloride. After 30 minutes, 10 ml of 10% potassium iodide solution is added and the whole left to stand for 5 minutes, after which liberated iodine is titrated with 0.1 N sodium thiosulfate (starch indicator). 1 ml of 0.1 N hydrochloric acid solution of iodine chloride corresponds to 0.0118 g of phanodorn.

Sodium Evipan. Satisfactory results were obtained on using variant "2" for the quantitative determination of sodium evipan. About 0.1 g of sodium evipan (accurately weighed) is dissolved in 5 ml of water, 30 ml of a 0.1 N hydrochloric acid solution of iodine chloride is added, and the whole left for 30 minutes. The liberated iodine is extracted with chloroform until the chloroform extract is colorless. The chloroform extracts are washed twice with 5 ml of water, which are in turn shaken up with chloroform.

The washed aqueous extracts are combined with the hydrochloric acid layer and 2 g of potassium iodide added; the liberated iodine is titrated with 0.1 N sodium thiosulfate (starch indicator). 1 ml of a 0.1 N hydrochloric acid solution of iodine chloride corresponds to 0.0064 g of sodium evipan.

Iodochlorometric Determination of Malil

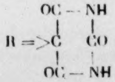
On addition of a 0.1 N hydrochloric acid solution of iodine chloride to an aqueous solution of malil, a copious precipitate is formed while the iodine chloride solution is decolorized.

As we have shown [9], this reaction consists in the combination of iodine chloride across the double bond of the allyl radicals and subsequent hydrolysis of the iodochloro derivative formed, this in turn is hydrolyzed to give the iodohydrin of barbituric acid; the reaction can be expressed as follows:

$$(CH_2{=}CH-CH_2)_2R + 2ICl \rightarrow (CH_2I-CHCl-CH_2)_2R;$$

$$(CH_2I-CHCl-CH_2)_2R + 2H_2O \rightarrow (CH_2I-CH(OH)-CH_2)_2R + 2HCl,$$

Where



$$R = {>}C\begin{matrix} OC-NH \\ | \qquad | \\ \;\; CO \\ | \qquad | \\ OC-NH \end{matrix}$$

The gram equivalent of malil is M/4. It is best to carry out the reaction in dilute solutions of malil (0.1 - 0.15%); the amount of hydrochloric acid solution of iodine chloride should be one and a half times the theoretical amount; under these conditions, the reaction is quantitative after only 5 minutes; 4 equivalents of iodine chloride are used while 2 equivalents of acid are liberated.

Experimental Procedure. About 0.1 g of malil (accurately weighed) is dissolved on heating in 100 ml of water; the solution is cooled and 30 ml of a 0.1 N hydrochloric acid solution of iodine chloride added. After standing for 5 minutes, 2 g of potassium iodide is added added and the liberated iodine titrated with 0.1 N sodium thiosulfate; starch solution is added towards the end point.

1 ml of 0.1 N hydrochloric acid solution of iodine chloride corresponds to 0.005005 g of malil.

Other barbiturates such as luminal and veronal, and also aspirin, phenacetin, antifebrin, do not interfere with the quantitative determination of malil. Antipyrin, pyramidone, and codeine do not interfere.

The results obtained are given in Table 2.

TABLE 2

Determination of Malil, Phanodorn, and Sodium Evipan by Means of a Hydrochloric Acid Solution of Iodine Chloride.

Preparation analyzed	Sample weight in g	0.1 N $Na_2S_2O_3$ solution used for total titration of iodine in ml	Amount of 0.1 N ICl solution combined, in ml	Barbiturate found		
				In g	In %	Amt. specified in VIIIth Pharmacopeia or other data
Malil	0.0438		8.37	0.0436	99.5	99.5
	0.0936		17.68	0.0931	99.5	
	0.0916		17.63	0.0917	100.1	
Phanodorn	0.0732	6.14		0.0725	99.0	99.2
	0.0944	8.00		0.0944	100.0	
Sodium evipan	0.0912		13.75	0.0888	97.4	97.5
	0.0887		13.38	0.0864	97.4	

The author wishes to thank Ya. A. Fialkov for valuable advice.

SUMMARY

An iodochlorometric method has been developed for the quantitative determination of barbiturates which contain unsaturated groups (malil, sodium evipan, and phanodorn) and for thiobarbituric acid derivatives (sodium thiopental) in admixture with sodium carbonate.

The application of the method described enables one to determine the preparation listed above in mixtures with other barbiturates (luminal, veronal), which do not react with a hydrochloric acid solution of iodine chloride.

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BRIEF COMMUNICATIONS

"IN SITU" METHOD OF DETERMINING ALUMINUM IN ALLOYS

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For rapid identification of aluminum in certain alloys, after the surface has been prepared, the new sensitive reagent arsenazo which has been proposed earlier for the quantitative determination of aluminum [1, 2] can be used; arsenazo is the sodium salt of benzene-2-arsonic acid < 1-azo-7 > -1,8 dihydroxynaphthalene-3,6-disulfonic acid. The sensitivity of the reaction for detecting aluminum is 0.05γ Al in 1 ml at a limiting dilution of 1:30,000,000 [3]. This reagent is also suitable for sorting some alloys, recognition of which is based on detection of aluminum. Tests were carried out with aluminum metal (99.9% Al) and duralumin. A drop of concentrated hydrochloric acid is placed on the metal surface which has been degreased and then cleaned with emery paper, and the acid is left in contact with the metal for 1-2 minutes. The acid is then washed off the surface with water (1.5 -2 ml), added dropwise from a pipet; the washings are collected in a porcelain basin, and the solution evaporated to dryness on asbestos placed on a hot plate. To the warm, dry, residue is added three drops of water, followed by one drop of concentrated hydrochloric acid and eight drops of a 0.005% aqueous solution of arsenazo. 8 drops of a 25% aqueous solution of urotropine is finally added from a dropper. A change in color from rose to violet indicates the presence of aluminum. A control test remains rose in color.

The reaction just described can also be used for distinguishing magnesium alloys type MA 5 (8-10% Al) from metallic magnesium. In the case of the latter, its aluminum content is insignificant and a negative result is given with arsenazo reagent.

"In situ" detection of aluminum can also be carried out in sulfuric acid media, in the case of the aluminum and magnesium alloys tested.

For detecting aluminum in nickel-aluminum alloys (4% and 10% Al), solution of some test material in situ is effected by placing a drop of aqua regia on the metal surface. The drop is washed off into a basin with water after 2-4 minutes contact. Subsequent procedure is the same as described above. It may be noted that metallic nickel (Mark 0000) does not give a reaction with arsenazo under the conditions which we used. On this basis it is possible to distinguish between alloys (Ni-Al ligatures) containing more than 4% Al and metallic nickel.

Aluminum can also be detected in iron and aluminum alloys (12% Al) under identical conditions, but only after reduction of trivalent iron with ascorbic acid (2 drops of a 10% solution before addition of arsenazo reagent).

A blank test should be carried out in all cases.

SUMMARY

Arsenazo (the sodium salt of benzene-2-arsonic acid < 1-azo-7 > 1,8-dihydroxynaphthalene-3,6-disulfonic acid) can be used for qualitative detection of aluminum in alloys, using the "in situ" method. It is possible by means of this reagent to distinguish between magnesium based alloys (8-10% Al) and metallic

magnesium; Ni-Al alloys and metallic nickel; Fe-Al alloys and pure ion; and aluminum based alloys (silumin, duralumin) and other alloys.

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A QUALITATIVE COLOR REACTION FOR ANTIMONY

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We have used diphenylcarbazide for detection of antimony in the presence of other elements. An alcoholic solution of diphenylcarbazide which has been partially oxidized by atmospheric oxygen proved to be a specific reagent for detection of trivalent antimony in hydrochloric acid media.

A freshly prepared 1% alcoholic solution of diphenylcarbazide gives a hardly perceptible rose-orange color with trivalent antimony ions in hydrochloric acid solution. A solution of diphenylcarbazide which is two or three days old, or has been made by bubbling air through a freshly prepared solution for half an hour, gives a pale orange color with antimony; on shaking, the organic solvent acquires a bright raspberry color. The color only develops with antimony in the presence of hydrochloric acid.

Hydrochloric acid concentration can be altered within the range 1 to 4 g-mol/ liter. Optimum acidity is 1-2 N.

A series of organic solvents were tested as extractants for the colored product: carbon tetrachloride, chloroform, ethyl ether, benzene, amyl alcohol, and a mixture of amyl alcohol and ethyl ether. Best results were obtained with amyl alcohol. For detection of trivalent antimony in hydrochloric acid in the presence of other cations which react with diphenylcarbazide, the amount of reagent is increased. In 1-2 N hydrochloric acid the reaction is specific for trivalent antimony. Under these conditions the following elements: tri-and sexivalent chromium, cadmium, divalent manganese, cobalt, nickel, magnesium, bismuth, copper, zinc, aluminum, and silver in amounts 100 times that of antimony do not interfere with the detection of antimony, while lead, ammonium, and iron in amounts 50 times that of the antimony do not interfere. Quadrivalent tin, which gives a similar color, interferes. In the presence of divalent tin the sensitivity of the reaction decreases because of the gradual decolorization of the solution. Consequently, considerably more of the reagent has to be added. Vanadium compounds give a yellow color with the reagent in hydrochloric acid solution; consequently vanadium when present in amounts which are ten times those of antimony also depresses the sensitivity. Nitric, sulfuric, and acetic acids destroy the color; when large amounts of phosphate ions are present, a large amount of hydrochloric acid is necessary.

Antimony can be detected as follows: into a small test tube are introduced one or two drops of the trivalent antimony solution, 5-10 drops of 1 N HCl, 10 drops of amyl alcohol, and one or two drops of the partially oxidized solution of diphenylcarbazide. When antimony is present, the upper layer of solvent acquires a bright raspberry color on shaking. The limit of identification is 2×10^{-5} g Sb.

When other cations are present, it is necessary to take 2-3 times more diphenylcarbazide.

Trivalent antimony can be detected by the spot technique in the absence of other ions. On a filter paper, moistened with a drop of the hydrochloric test solution, is placed a small drop of 1% alcoholic solution of partially oxidized diphenylcarbazide. A bright raspberry spot develops in the presence of trivalent antimony.

SUMMARY

A 0.01 N alcoholic solution of diphenylcarbazide which has been partially oxidized by air gives a raspberry color with trivalent antimony in hydrochloric acid media. The color can be extracted with amyl alcohol.

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BROMINE-HELIANTHIN METHOD FOR DETERMINING MANGANESE IN HIGH ALLOY STEELS AND IN DURALUMIN

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MnO_4^- ions are readily oxidized by bromine ions Br^- even in weakly acid media, while both $Cr_2O_7^{2-}$ ions and the ions of other components of steel are either only oxidized with difficulty by Br^- ions, or are not oxidized at all, even in the most acid media [1, 2]. The bromine which is liberated during oxidation can be titrated in 0.1-3 N H_2SO_4 with an aqueous solution of helianthin (Methyl Orange).

Helianthin [3] and other azo dyes can behave both as oxidizing and reducing agents. Thus, helianthin has been used as an oxidizing agent for determination of tin in ores [4], and as a reducing agent for determining chlorine [5-8]. The bromination products of helianthin give a bright yellow color to the solution. Theoretically one molecule of helianthin should be equivalent to two bromine atoms. We found that in fact one gram molecule of helianthin is equivalent to 2.15-2.17 g.atoms of bromine. Other research workers [5,7] have also noted the absence of a strictly stoichiometric relation during the action of chlorine and bromine on helianthin; this must be borne in mind when standardizing helianthin solution.

The method we have developed has been checked both on solutions of $KMnO_4$ (in the absence and in the presence of elements which interfere during manganese determinations) as well as on standard samples from the Ural Institute of Ferrous Metals. Manganese was oxidized to the septivalent state by the persulfate-silver method; the amount of silver nitrate added was however much less [9], 25-50 times less, than that indicated in GOST [10]. Manganese can also be oxidized by the persulfate-cobalt method [1, 2]. An approximately 0.4% aqueous solution of helianthin was used as standard. The strength of such a solution remained constant over a considerable period (3-4 months). The helianthin solution was standardized against a standard sample of steel type 10b, or some other alloy in which manganese is to be determined.

The dichromate ion, particularly at high concentrations (Mn:Cr = 1:400), even when the acidity is higher than 1 N with respect to H_2SO_4 reacts to an appreciable extent with bromide ions. During determination of manganese in the presence of large amounts of chromium, the acidity of the solution should not be higher than 1 N with respect to H_2SO_4 [11]. Vanadate ions start to oxidize bromide ions appreciably at acidities greater than 7 N with respect to H_2SO_4 [12-13]. In the presence of large amounts of chromium (greater than 40%) and cobalt (greater than 50%), when the sample weight used is 0.2 g, establishment of the end point is very difficult. The color of the remaining ions has no essential effect.

Analytical Procedure. 0.2 g of sample is taken for analysis of alloys with manganese contents ranging from 0.1 to 1.5%. Cast iron, steels (simple and low alloy), and duralumin are dissolved in 20-30 ml of acid mixture (200 ml H_2SO_4 sp.gr. 1.84 + 50 ml H_3PO_4 sp.gr. 1.62 and the volume made up to a liter). High alloy steels (tungsten-vanadium, and cobalt steels* etc.) are dissolved in 20-30 ml acid mixture (250 ml H_2SO_4 sp.gr. 1.84 + 200 ml H_3PO_4 sp.gr. 1.62 and the volume made up to a liter). Stainless steels are dissolved in 20-30 ml H_2SO_4 (1:5). Nichrome is dissolved in about 10 ml of aqua regia or concentrated HCl. When the sample of nichrome has dissolved, 20 ml of H_2SO_4 (1:5) is added and the solution evaporated until white fumes appear. Brasses and bronzes are dissolved in 25-30 ml HNO_3 (2:3).

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* It is recommended that 5 ml of 1 M $(NH_4)_2S_2O_8$ solution be added before addition of HNO_3 for accelerating dissolution of cobalt-tungsten steels.

When the sample has dissolved, and when nitric acid has been used either on its own or in a mixture with other acids, concentrated HNO_3 is added dropwise until foaming ceases and the solution becomes clear; heating is then continued to remove nitrogen oxides. The volume of the solution is made up with distilled water (heated up beforehand to economize on time) to 100 ml and the solution heated to 80°; 2-4 drops of 0.1 N silver nitrate is then added* followed by 10-30 ml of a 1 M solution of ammonium persulfate. The solution is heated until the ammonium persulfate starts to break down vigorously; the solution is then removed from the hot plate and left in a warm placed until the decomposition of excess ammonium persulfate is almost complete. The solution is cooled under the tap and diluted to 1.5-3 times its volume with distilled water until the concentration of H_2SO_4 is 1.5 N; when there is a considerable amount of chromium dilution is adjusted to a give concentration not greater than 1 N. 2-5 ml of 10% solution of potassium bromide is added and when the color of the permanganate has disappeared, the liberated bromine is titrated with helianthin solution immediately (as fast as possible at the beginning of titration and then slower towards the end) until a rose or rose-orange color is obtained which does not disappear for one minute.

One determination takes 25-30 minutes.

The method has been checked under production conditions.

SUMMARY

Bromine ions are readily oxidized by MnO_4^- even in a weakly acid medium whereas Br^- is oxidized either with difficulty or not all by $Cr_2O_7^{2-}$ ions, or by ions of other components of steel, even in more acid media.

Bromine liberated during oxidation can be titrated in 0.1 N-3 N H_2SO_4 with an aqueous solution of helianthin.

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* Depending on the manganese and chromium contents.

** [Original Russian pagination. See C. B. translation.]

RAPID METHODS OF MICRO-ELEMENTAL ANALYSIS

PART 13. SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, SILICON AND SULFUR IN SULFUR-CONTAINING ORGANOSILICON COMPOUNDS

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Simultaneous determination of carbon, hydrogen, silicon, and sulfur in sulfur-containing organosilicon compounds would appear to be a logical extension of the methods we have developed earlier for simultaneous determination of carbon, hydrogen, and silicon, and of carbon, hydrogen, silicon, and halides [1, 2].

Thermal decomposition of sulfur-containing organosilicon compounds under rapid combustion conditions in a rapid stream of oxygen occurs with formation of some silicon carbide; i.e. the process is similar to that which happens in the case of compounds containing carbon, hydrogen, and silicon. Consequently, during analysis of such compounds, decomposition should be carried out in the presence of chromium oxide on asbestos, as indicated for compounds containing C, H, and Si [1]. Chromium oxide does not prevent formation of sulfur oxides and the latter can accordingly be trapped and determined by the Korshun-Sheveleva method [3], by means of silver heated to 700° in a special apparatus. Finely dispersed silica is quantitatively trapped in the vessel used for decomposition by the asbestos catalyst. Nitrogen, when present, does not interfere. The method is simple and convenient. Results of determinations are given in the Table. The accuracy of determination for each element lies within the limits of ± 0.3%.

SUMMARY

A method has been developed for simultaneous determination of C,H, Si, and S in sulfur-containing organosilicon compounds.

Experimental error for each element is within the limits of ± 0.2 to 0.3%.

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* Original Russian pagination. See C.B. translation.

Test compound	C in % Found	C in % Calculated	C Δ in %	H in % Found	H in % Calculated	H Δ in %	Si in % Found	Si in % Calculated	Si Δ in %	S in % Found	S in % Calculated	S Δ in %	Sample weight, in mg
α-Thiocyanoethyltrimethylsilane $(CH_3)_3SiCH(CH_3)SCN$	45.29	45.23	+0.06	8.33	8.22	+0.11	17.67	17.63	+0.04	19.80	20.13	−0.33	9.31
	45.35		+0.12	8.33		+0.11	17.42		−0.21	20.06		−0.07	11.83
β-(Trimethylsilylmethylmercapto)-propionitrile $(CH_3)_3SiCH_2SCH_2CH_2CN$	48.65	48.50	+0.15	8.87	8.72	+0.15	16.16	16.20	−0.04	18.80	18.50	+0.30	10.12
	48.42		−0.08	8.77		+0.05	16.28		+0.08	18.66		+0.16	8.93
	48.55		+0.05	8.67		−0.05	16.46		+0.26	18.79		+0.29	11.44
α-Thiocyanomethyldiphenylmethylsilane $CH_3(C_6H_5)_2SiCH_2SCN$	67.09	66.88	−0.21	5.67	5.60	+0.07	10.15	10.42	−0.27	11.94	11.90	+0.04	12.39
	66.95		+0.07	5.61		+0.01	10.28		−0.14	12.03		+0.13	10.41
1,2-Di(α-thiocyanoethyl)tetramethyldisiloxane $O(Si(CH_3)_2CH_2SCN)_2$	34.80	34.75	+0.05	5.94	5.83	+0.11	20.02	20.31	−0.29	23.21	23.16	+0.05	11.22
	34.80		+0.05	5.82		−0.01	20.35		+0.04	23.35		+0.19	10.61
	34.63		−0.12	5.76		−0.07	19.95		−0.36	23.59		+0.43	11.12
β-(Methyldibutylsilymethylmercapto) propionitrile $CH_3(C_4H_9)_2SiCH_2SCH_2CH_2CN$	60.98	60.63	+0.35	10.47	10.57	−0.10	10.67	10.91	−0.24	12.23	12.45	−0.22	9.42
	60.73		+0.10	10.57		0.00	10.57		−0.34	12.40		−0.05	11.63
	60.40		−0.23	10.79		+0.22	10.75		−0.16	12.42		−0.03	10.22
Bis-(α-thiocyanomethyl) dimethylsilane $NCSCH_2Si(CH_3)_2CH_2SCN$	35.69	35.61	+0.08	5.02	4.98	+0.04	13.70	13.88	−0.18	31.99	31.69	+0.30	9.62
	35.63		+0.02	4.95		−0.03	—			31.54		−0.14	12.83
	35.65		+0.04	5.01		+0.03	13.61		−0.27	31.57		−0.12	13.06
α-(Thiocyanomethyl) methyldipropylsilane $CH_3(C_3H_7)_2SiCH_2SCN$	53.57	53.66	−0.09	9.62	9.51	+0.11	14.15	13.95	+0.20	15.77	15.92	−0.15	10.27
	53.56		−0.10	9.53		+0.02	14.13		+0.18	16.05		+0.13	12.27
α-Thiomethyldiethylmethylsilane $CH_3(C_2H_5)_2SiCH_2SH$	48.86	48.58	+0.28	10.89	10.87	+0.02	19.01	18.93	+0.08	21.58	21.62	−0.04	9.02
	48.79		+0.21	10.99		+0.12	19.16		+0.23	21.79		+0.10	11.73
β-(Trimethylsilyl-γ-propylmercapto) propionitrile $(CH_3)_3Si(CH_2)_3SCH_2CH_2CN$	53.64	53.66	−0.02	9.56	9.51	+0.05	13.82	13.95	−0.13	16.02	15.92	+0.10	9.56
	53.87		+0.21	9.63		+0.12	13.87		−0.08	16.15		+0.23	9.20
β-(Methyldiethylsilymethylmercapto) propionitrile $CH_3(C_2H_5)_2SiCH_2SCH_2CH_2CN$	53.68	53.66	−0.02	9.44	9.51	−0.07	13.81	13.95	−0.14	15.69	15.92	−0.23	10.32
	53.63		−0.03	9.47		−0.04	13.63		−0.32	15.87		−0.05	10.56
γ-(Thiocyanopropyl) trimethylsilane $(CH_3)_3SiCH_2CH_2CH_2SCN$	48.40	48.50	−0.10	8.49	8.72	−0.23	16.43	16.20	+0.23	18.52	18.50	+0.02	14.35
	48.56		+0.06	8.75		+0.03	16.27		+0.07	18.61		+0.11	7.84

THE INTRODUCTION OF RAPID METHODS OF MICRO-ANALYSIS INTO INDUSTRIAL PRACTICE

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The new water soluble analog of Vitamin K, "Vikasol" $C_{11}H_8O_2 \cdot NaHSO_3$, prepared by Academician A. V. Palladin [1], is the bisulfite derivative of 2-methyl-1,4-naphthoquinone.

The correctness of the formula indicated above has been confirmed by determination of the sodium content alone. In order to control the quality of preparations of this material, simultaneous determination of all four elements on one aliquot by methods developed by Korshun and coworkers is of particular interest, in particular, their method of rapid combustion in an empty tube [9].

For simultaneous determination of sodium, sulfur, carbon, and hydrogen, combustion of Vikasol was carried out at a slow rate over a period of 30-40 minutes using the colorless burner flame, and with an oxygen throughput of 30 ml/minute. The vessel used for holding the sample was lengthened to 80 mm while its internal diameter was 5-6 mm. It was found to be essential that combustion proceeded gradually, and was completed within the combustion vessel. By moving the burner flame backwards and forwards several times from the containing vessel, the reaction sphere could be enriched with oxygen, thereby ensuring complete combustion of the carbonized part of the sample. Towards the end of the determination, the burner flame was increased. Carbon and hydrogen were trapped as usual, while sodium remained as the sulfate in the combustion vessel. The infusibility and the low volatility of the Na_2SO_4 meant that combustion could be carried out without an internal absorbent or asbestos catalyst or asbestos tubes. Under the conditions used, the sodium contained as bisulfite in the original material was converted into Na_2SO_4 all of which remained in the combustion vessel. *

The bisulfite sulfur of Vikasol was found in two places: part of it was trapped by metallic silver in the quartz apparatus as Ag_2SO_4, while the other half of the sulfur remained as Na_2SO_4 in the combustion vessel.

During simultaneous determination of sodium, sulfur, carbon, and hydrogen in a series of Vikasol preparations, results were obtained which were in good agreement with each other; these indicate that the Vikasol was fairly homogenous with respect to composition. Nevertheless, results of some samples of Vikasol indicated that they contained three molecules of water and had a formula corresponding to $C_{11}H_8O_2 \cdot NaHSO_3 \cdot 3H_2O$ (calculated values 40.00% C, 4.54% H, 9.69% S and 6.97% Na). In some cases preparations were obtained with two molecules of water.

It is possible, using this method, to establish the amount of sodium bisulfite in excess in Vikasol preparations.

SUMMARY

A rapid method for micro-analysis of Vikasol has been developed; it is based on simultaneous determination of carbon, hydrogen, sodium, and sulfur by combustion in an empty tube. One determination takes one hour. The method can be used for controlling Vikasol production.

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* Tests in which chemically pure Na_2SO_4 was heated were used as control tests. In all cases the amount of Na_2SO_4 after test was the same as the original amount taken.

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CHRONICLE

ROSTISLAV PETROVICH LASTOVSKY

(On his Fiftieth Birthday)

On the seventh of March 1957 Professor Rostislav Petrovich Lastovsky, one of our outstanding chemists, and a doctor of chemical sciences, celebrated his fiftieth birthday and his twenty-fifth year of scientific and teaching activity.

In 1930, Lastovsky, after finishing in the D.I. Mendeleev Moscow Chemico-Technological Institute, where he had specialized on aniline dyes, went to work in the K.E. Voroshilov Institute of Organic Intermediates and Dyes. He also remained as assistant in the chair of analytical chemistry in the Mendeleev Institute headed by Professor Ya. I. Mikhailenko.

He remained at the Voroshilov Institute from 1930 to 1947, first as young scientific coworker, and finally as head of the analytical laboratory and one of the synthesis laboratories.

In 1940, at the Mendeleev Institute, Lastovsky defended his thesis for a degree of Candidate of Chemical Sciences, while in 1947 he defended his doctor's thesis on the chemistry of urea and its derivatives.

Since 1947, Lastovsky has been the deputy director (on the scientific side) of the All-Union Scientific Research Institute of Chemical Reagents where he works at present.

Simultaneously with his scientific work Lastovsky also carried on with his teaching activity in a number of higher educational institutions in Moscow. He was made professor in 1948 and from 1948 to 1955 was head of the chair of Chemistry in the All-Union Correspondence Course Institute of Soviet Trade.

During the last 10 years, working at the All-Union Scientific Research Institute of Chemical Reagents, he devoted a lot of energy to organizing scientific research work, and started a series of investigations on developing new methods of preparing and analyzing inorganic and organic materials of a high degree of purity, and also to extend the variety of reagents issued by Russian chemical industry.

His scientific interests are widespread and varied. His work on urea derivatives, chemical analysis of intermediates and dyes, syntheses and studies of organic reagents and their stabilization have been particularly fruitful.

During his scientific work, Lastovsky, in conjuction with coworkers, has carried out more than 70 studies, part of which has appeared in candidates' theses; these have contributed greatly to the knowledge and production of intermediates, reagents, special chemicals, and to the knowledge of methods of plant control. Of his published work, particular mention should be made of "Technical Analysis of Intermediates and Dyes". This book has been translated into Czech and has received acclaim from workers in Russia and abroad.

Lastovsky has devoted considerable attention to educating new cadres of Soviet specialists reading quantitative analysis, organic chemistry, and dye-stuffs chemistry.

He is an active member of the Analytical Commission of the USSR Academy of Sciences, and a member of the Scientific Council of the V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry.

His services have been recognized by a number of awards: The Order of Lenin, The Red Banner, and three medals.

A STUDY OF THE MECHANISM OF COPRECIPITATION OF CATIONS WITH SULFIDES BY MEANS OF RADIOACTIVE ISOTOPES

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Coprecipitation of cations of the third analytical group with sulfides of the hydrogen sulfide group has been studied by many research workers. Various hypotheses have been advanced to explain this phenomenon [1]. All the same, this process is very complicated and has many aspects which have not been hitherto explained. The most widely spread hypothesis – one which has entered into text books on chemical analysis – is that of Kolthoff and his coworkers; according to this hypothesis, attraction of third group cations by group two sulfides proceeds as the result of subsequent precipitation caused by HS^- and S^{2-} ions adsorbed on the strongly developed surface of the original precipitates. The concentration of HS^- and S^{2-} ions on the surface of the sulfide precipitates which have separated out is greater than that in solution, as a result of which cations of the third group separate out; whereas, the latter under the precipitation conditions used (0.3 N HCl) should remain completely in solution.

The experiments which we carried out showed that the part played by the surface is more complicated than is normally assumed. The accepted opinion regarding the capacity of sulfide precipitates which have a large surface to be contaminated cannot be extended to all cases of coprecipitation of group three cations with second group sulfides. It has been established that coprecipitation of small amounts of zinc with HgS, CdS, and SnS_2, is expressed to a strong degree; while in the case of the other sulfides (Ag_2S, PbS, As_2S_3, and Sb_2S_3) coprecipitation of zinc is insignificant. Further, while a rate of saturation of the solution with hydrogen sulfide, which favors formation of a precipitate with a large surface leads, in the case of HgS, CdS, and SnS_2, to a large increase in coprecipitation, in the case of the sulfides Ag_2S, PbS, As_2S_3, and Sb_2S_3 this rate is of no significance [2].

These facts served as a basis for pursuing a study of aging of sulfides, and of those changes in structure and surface which occur during aging. Since attraction of cations by sulfide proceeds preferentially after their formation, carrying out such an investigation should give a clearer picture of the mechanism of the phenomenon of coprecipitation, and the part played in this process by the surface and the changes which occur during aging of sulfides. To do this a study was made of the kinetics of sorption of surface active dyes by hydrogen sulfide group sulfides, while changes in the structure during aging of sulfides were studied with the aid of an electron microscope and electronograph.

Experiments showed that sorption of surface active dyes is sharply expressed for all hydrogen sulfide group sulfides. Calculations of the specific surface of precipitates of the compounds indicated gave a large value (about 600 meter^2). Accordingly, the reason for a large difference in coprecipitation, e. g. of zinc, with various sulfides, is incomprehensible when one starts from the explanation given above about the presence of HS^- and S^{2-} ions on the strongly developed surface of the sulfides.

It was also found that in the case of certain sulfides (HgS, Sb_2S_3, SnS_2, and Bi_2S_3), during their aging, the amount of absorbed dye increases, while in the case of others (CuS, Ag_2S) it decreases. Sorption of dyes by precipitates of CdS, As_2S_3, and PbS hardly changes at all with time [3]. Since absorption of dyes depends on effective sorbing surface and its area, it was natural to assume that particles of group one sulfides should break down with time into smaller particles with a consequent increase in total surface. In the case of group two sulfides, on the other hand, aggregation of particles should be observed, and consequently, a decrease in surface area; in the case of group three sulfides no appreciable changes should occur. These assumption were confirmed during a study of sulfide structure during aging, both in the experiments indicated above and in those described in the present article.

If one starts from the premise that coprecipitation of ions with sulfides depends on the surface of the precipitates, then the nature of the change in the amount of coprecipitated cation or sorbed dye should be expressed by similar curves. In order to establish whether this assumption corresponds to reality and to determine the role of the surface in the given instance, we studied coprecipitation of thallium, indium, and gallium* with HgS, CuS, and CdS. As indicated above, during aging of HgS and CuS, the effective surface of the first sulfide increases, while that of the second decreases. In the case of CdS, the surface hardly changes at all during aging. Consequently, these three sulfides were chosen for investigation.

A comparative study of the coprecipitation of gallium, indium, and thallium is interesting from the point of view that their chemical properties change regularly with increasing atomic weight.

Furthermore, it is possible to compare results on the coprecipitation of Ga^{3+}, In^{3+}, and Tl^{+} with the solubility of their sulfides, and also to compare their capacity to give mixed crystals with HgS, CuS, and CdS.

Simultaneously with determination of the extent of coprecipitation of the metals indicated above, a study was made of changes in the structure of the sulfides of mercury, copper, and cadmium which occur during aging, by means of an electron microscope and an electronograph.

EXPERIMENTAL

Starting Materials

0.1 M solutions of the chlorides of mercury, copper, and cadmium and 0.03 M solutions of the nitrates of gallium, indium, and thallium were used for our experiments. The radioisotopes Ga^{72} ($T^{1/2}$ = 14.25 hours); In^{114} ($T^{1/2}$ = 49 days); Tl^{204} ($T^{1/2}$ = 2.7 years)** were purified and checked for radiochemical purity by determining the half-life period.

Experimental Procedure

Into a 150 ml flask was introduced 1 ml of a solution of $HgCl_2$, $CuCl_2$, or $CdCl_2$. Gallium, indium, and thallium were introduced in amounts of 2, 3.28, or 5.86 mg respectively. In this way, the metals indicated were taken in equimolar amounts. Hydrochloric acid concentration was 0.3 N while total volume of solution was 100 ml. A mechanical stirrer was used for stirring the solution (about 600 revolutions/minute), and a stream of H_2S (about 500 cm^3/minute) bubbled for 5 minutes through the solution kept at 20 - 25°***.

The mixtures were centrifuged after the time intervals given in Tables 1 - 3. After separation of precipitates from mother liquor and after they had been washed six times with 1% NH_4NO_3 saturated with H_2S, they were dissolved in 5 - 6 ml of concentrated HNO_3 (CuS, CdS) or a mixture of HNO_3 + HCl (HgS). The solutions obtained were transferred to watch glasses 7 cm in diameter and evaporated on a water bath. The activities of the samples were determined on a B-2 setup. In those cases where coprecipitation was high (80 - 100%) the activity of both precipitate and filtrate was determined. Control (blanks) tests were carried out under identical conditions, taking into account the screening action of the salts on the radiation, and correcting for break down. Percentage coprecipitation was determined by comparing the activity of test samples and that of standards.

3 - 5 replicates were carried out to determine percentage coprecipitation.

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* With respect to the solubility of their sulfides in acids, gallium, indium, and thallium can be related to the third group of metals.

** [As in original. Publisher's note.]

*** Preparation of the H_2S used has been described in [4].

The structure of the sulfides• was studied with the aid of a 100 kilovolt electron microscope type EM-100 which gave a magnification of 12,000. The resolving distance was about 100 A; the voltage 84 kilovolts. After micro-photographs had been taken, electronograms were taken with the same preparation. Sulfides were separated under the same conditions as those used in experiments on the study of coprecipitation of gallium, indium, and thallium. Sulfides were aged for 2 and 24 hours, and washed 4 times with distilled water. Water was added to the precipitate and after the test tubes had been shaken, 5 - 6 samples were taken by means of a fine capillary, and transferred onto a collodion film with nickel grids; the latter were than dried at 25° and studied under the electron microscope and electronograph.

Coprecipitation of Gallium with HgS, CuS, and CdS

Preliminary tests showed that the amount of gallium attracted by HgS decreases with time, while in the case of CuS and CdS the amount increases; subsequently, a systematic study was made of coprecipitation of gallium with the sulfides indicated above after various time intervals. Experimental results are given in Table 1 while they are graphically represented in Fig. 1. For comparison, in Fig. 2 are given curves which illustrate the kinetics of sorption of Neutral Red by the sulfides HgS, CuS, and CdS••. Micro-photographs of these sulfides and electronograms are given in Fig. 3.

TABLE 1

Coprecipitation of Gallium with HgS, CuS, and CdS in Relation to the Time the Precipitate is left in Contact with Solution

Rate of saturation with hydrogen sulfide about 500 cm^3/minute while the solution is being stirred at the rate of 600 revolutions/minute; temperature 20 - 25°.

Metal sulfide MeS	Amount of MeS, in mg	Amount of Ga, in mg	Ratio Ga^{3+}: :Me^{2+}	Gallium coprecipitated, in %, after					
				¼ hr.	4 hr.	12 hr.	24 hr.	28 hr.	48 hr.
HgS	232.7	2	1:34.8	19.9	14.1	8.5	5.8	—	3.9
CuS	95.6	2	1:34.8	0.53	—	6.2	14.3	—	11.9
CdS	144.5	2	1:34.8	2.9	—	7.5	12.3	10.5	11.3

From these results it is clear that coprecipitation of gallium in the first stage is high only in the case of HgS; coprecipitation with CuS and CdS is insignificant; it increases with time.

Of the greatest interest is the change in percentage coprecipitation of gallium with aging of the sulfides indicated.

A comparision of the curves (Figs. 2 and 1) shows that with time, sorption of Neutral Red, and consequently the surface of the HgS, increases. Meanwhile, coprecipitation of gallium during aging of HgS decreases. The amount of gallium attracted by CuS and CdS increases with time, although the effective surface of the first sulfide increases, while that of the second does not change. One can also assess the character of changes in the surface during aging of HgS, CuS, and CdS by examining microphotographs and electronograms.

In accordance with results on the increase in effective sorbing surface of HgS, micro-photographs 1 and 2 and electronograms 3 and 4 (Fig. 3) show that during aging of this sulfide, there occurs disaggregation of its particles and a decrease in their size.

Cupric sulfide during aging is subject to aggregation, as micro-photographs 5 and 6 (Fig. 3) show. The increase in size of particles of this sulfide is evident from a comparison of electronograms 7 and 8 (Fig. 3). The decrease in sorption capacity of cupric sulfide during aging also testifies to a decrease in the effective surface of the given precipitate.

• This part of the work was carried out in Yu. M. Kushnir's laboratory; L. I. Zemlyanova carried out the work and we wish to thank her for this.

•• Results for HgS and CuS are taken from [3], while those for CdS are new results.

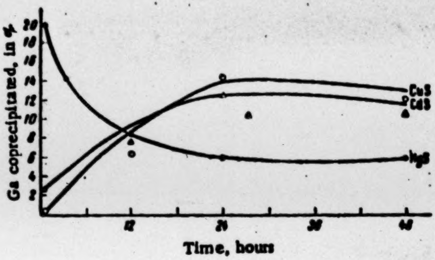

Fig. 1. Coprecipitation of gallium with HgS, CuS, and CdS in relation to time.

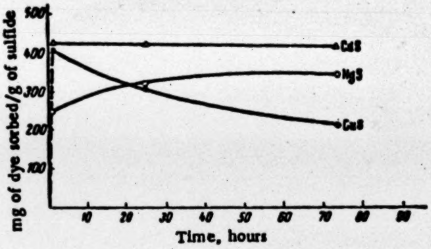

Fig. 2. Sorption of Neutral Red by HgS, CuS, and CdS in relation to time

The size of cadmium sulfide particles hardly changes at all on aging, as micro-photographs 9 and 10 (Fig. 3) show; this agrees with the fact that there is no change in effective sorptive area (Fig. 2). On the other hand, from the electronograms there is evident a more clearly defined diffraction picture for precipitates which have been aged. This indicates an increase in the particle size of cadmium sulfide crystals. Consequently, crystals of CdS precipitates which are shown in Fig. 3 (9 and 10) are aggregates of smaller crystals about the growth of which one can judge from electronograms 11 and 12.

Coprecipitation of Indium and Thallium with HgS, CuS, and CdS

During studies on coprecipitation of indium and thallium with HgS, CuS, and CdS, solutions of the metals were used which were equimolar with respect to 7.334 mg of gallium nitrate. The remaining conditions were the same as those in the experiments with gallium.

Results are given in Tables 2 and 3 and in Figs. 4 and 5.

A comparison of the results given in Tables 2 and 3 with those given in Table 1, and of Figs. 4 and 5 with Fig. 1. shows that indium behaves towards CdS and CuS in the same way as gallium. The difference is in the greater capacity of indium to coprecipitate. This is particularly the case with cupric sulfide. It is of interest to note that indium coprecipitates practically completely with HgS, and does not go into solution on aging. The fact that it does this is presumably linked with the considerably lower solubility of In_2S_3 in hydrochloric acid as compared with that of Ga_2S_3 in this acid.

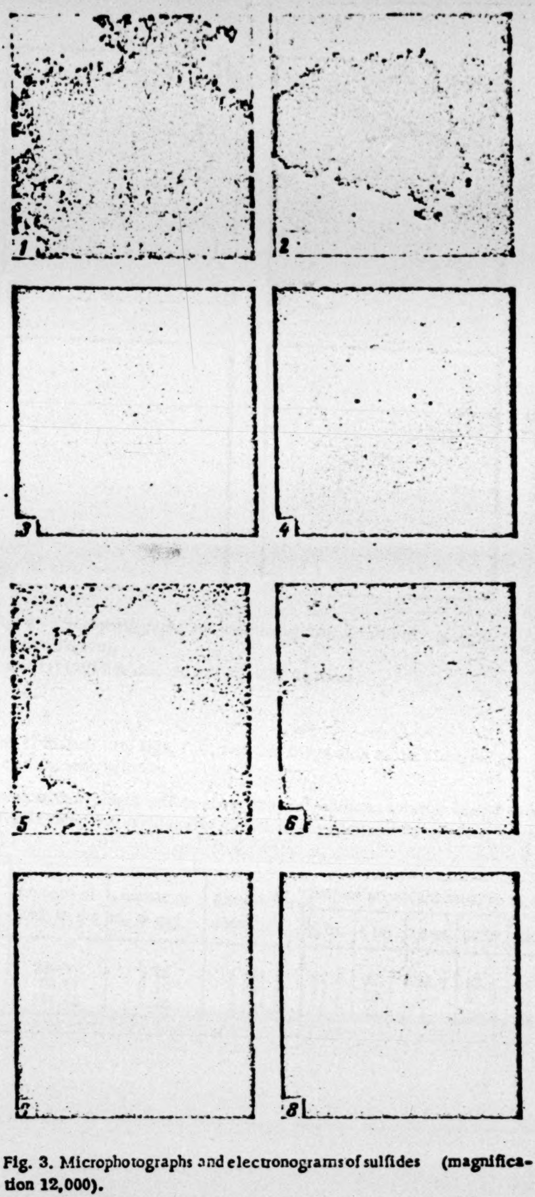

Fig. 3. Microphotographs and electronograms of sulfides (magnification 12,000).
1 and 3) HgS 2 hours; 2 and 4) HgS 24 hours; 5 and 7) CuS 2 hours; 6 and 8) CuS 24 hours.

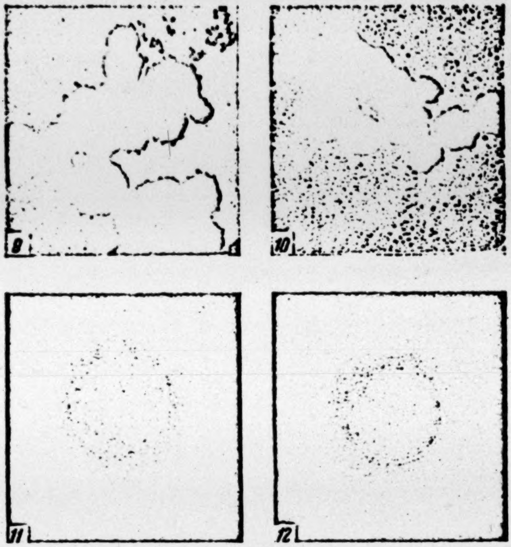

Fig. 3. Microphotographs and electronograms of sulfides (magnification 12,000).
9 and 11) CdS 2 hours; 10 and 12) CdS 24 hours.

TABLE 2

Coprecipitation of Indium with HgS, CuS, and CdS in Relation to the Time the Precipitate is in Contact with Solution

Rate of saturation with hydrogen sulfide about 500 cm^3/minute; solution stirred with a stirrer rotating at about 600 revolutions/minute in the course of 15 minutes; temperature 20 - 25°.

Metal sulfide MeS	Amount of MeS, in mg	Amount of In, in mg	Ratio In^{3+} : Me^{2+}	Indium coprecipitated, in %, after				
				¼ hr.	4 hr.	18 hr.	24 hr.	48 hr.
HgS	232.7	3.28	1 : 34.8	91.4	93.7	94.7	93.1	94.4
CuS	95.61	3.28	1 : 34.8	14.2	22.2	—	55.7	93.1
CdS	144.48	3.28	1 : 34.8	19.2	25.7	—	26.5	28

TABLE 3

Coprecipitation of Thallium with HgS, CuS, and CdS in Relation to the Time the Precipitate is in Contact with Solution

Rate of saturation with hydrogen sulfide about 500 cm³/minute; solution stirred with a stirrer rotating at about 600 revolutions/minute in the course of 15 minutes; temperature 20 - 25°

Metal sulfide MeS	Amount of MeS, in mg	Amount of Tl, in mg	Ratio Tl^{3+}: $:Me^{2+}$	Thallium coprecipitated, in %, after				
				¼ hr.	4 hr.	18 hr.	24 hr.	48 hr.
HgS	232.7	5.86	1 : 34.8	28.2	21.8	21.6	—	19.0
CuS	95.61	5.86	1 : 34.8	82.0	76.4	79.7	76.6	75.8
CdS	144.48	5.86	1 : 34.8	56.4	38.9	29.1	26.4	30.1

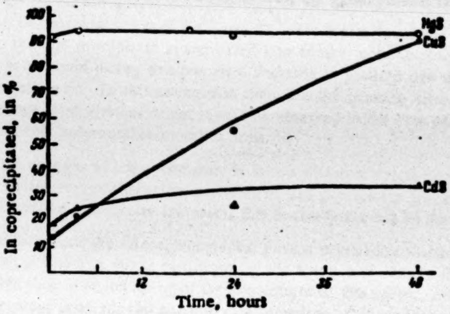

Fig. 4. Coprecipitation of indium with HgS, CuS, and CdS in relation to time.

Thallium is strongly coprecipitated with CuS, and with time its content in the precipitate does not change (analogous to the case of coprecipitation of indium with HgS). In the case of CdS and HgS trapping of thallium is weaker and decreases on aging. The behavior of thallium towards HgS is similar to the behavior of gallium; on aging, coprecipitation decreases. Nevertheless, coprecipitation of thallim with CdS proceeds differently; in this connection, it occupies a special position, this being related, presumably, to differences between its properties and those of gallium and indium.

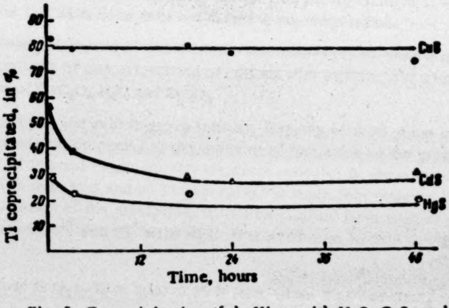

Fig. 5. Coprecipitation of thallium with HgS, CuS, and CdS in relation to time

Discussion of Results

The study of the kinetics of coprecipitation of gallium, indium, and thallium ions with HgS, CuS, and CdS in relation to changes in the structure and surface of the latter which occur during aging, has enabled us to get a more complete picture of the processes which occur, and to establish some of the laws governing these processes. As the results of electronic microphotography and diffraction patterns show, during aging of HgS, breakdown of precipitate particles is observed. The increase of the effective surface of the precipitate on aging also points to this.

The decrease in size of HgS particles which is connected with aging causes coprecipitated Ga^{3+} and Tl^{+} to go into solution despite the increase in total surface of the precipitate. This phenomenon is caused by recrystallization with a transformation into another modification of HgS, and by decrease in particle size.

The amount of indium coprecipitated with HgS remains constant on aging; this can be explained by the considerably lower solubility of In_2S_3 in HCl as compared with that of Tl_2S and Ga_2S_3*. The sulfides of univalent thallium and trivalent gallium which are trapped during the first stage of the coprecipitation process, return into solution again under the influence of 0.3 N HCl when the HgS particles break down. In the case of In_2S_3 however, in view of the considerably lower solubility of this sulfide in HCl, the given process is not observed.

A study of the kinetics of coprecipitation of Ga^{3+} and Tl^{+} with mercuric sulfide is interesting from the point of view that on aging, the HgS precipitate is converted into another polymorphic modification. As the electronogram shows, there is observed during this process a decrease in particle size to such an extent that no clear diffraction patterns are observed. In this connection therefore the question arises as to whether this phenomenon is of general significance, and whether or not it will be observed in the case of other sulfides which are also capable of changing over into polymorphic modifications.

Aging and the structural changes which accompany it take a different course in the case of CuS and CdS than in the case of HgS. During recrystallization, particles of CuS precipitate increase in size and form aggregates. The total surface of the precipitate increases; this is also borne out by the small sorption of the dye.

CdS particles, as is evident from the microphotographs, have a crystalline structure and their particle size hardly changes at all on aging (24 hours); this is confirmed by the absence of changes in effective surface. Nevertheless, electronograms of CdS show that, on aging of the precipitate of this sulfide, crystallization of the particles occur, their structure becomes ordered, and particle size increases. CdS particles which are visible under the electron microscope and have a particle size of 5×10^{-5} cm, are aggregates of smaller crystals whose size, according to the width of the diffraction rings, can be approximately calculated to be 10^{-6} cm. Calculations show that a particle of CdS visible under the electron microscope contains about 25,000 smaller particles. This explains the fact that despite the absence of changes in the surface of particles which are visible under the electron microscope, coprecipitation increases on aging.

During determination of the percentage coprecipitation of Ga^{3+}, In^{3+}, and Tl^{+} with CuS and CdS, it was found that aging of these sulfides leads to a further trapping of cations of gallium and indium by the precipitates (thallium behaves differently towards CdS). This is explained by recrystallization of precipitates of CuS and CdS and the growth of the particles during the time when coprecipitation occurs. It is essential to point out however, that the sorbing surface of the CuS decreases, while that of CdS hardly changes at all; it is possible to conclude from this that the decrease in CuS surface does not decrease coprecipitation.

Results of these investigations and of those carried out earlier [1, 2], enable one to put forward some general ideas regarding the phenomenon of coprecipitation of cations with sulfides, and also with typically crystalline precipitates, such as those of $CaC_2O_4.H_2O$ and $BaSO_4$.

During deposition of hydrogen sulfide group sulfides, trapping of third group cations is observed to varying extents in all cases. Coprecipitation occurs at the moment of formation of the precipitates, and subsequently during aging, the amount of trapped cation usually increases strongly; in some cases it hardly changes at all (during coprecipitation of In with HgS and of Tl with CuS). It is possible, however, to observe another phenomenon – during recrystallization of the precipitate it will be purified from trapped cations. This takes place e.g. during coprecipitation of Ga^{3+} and Tl^{+} with HgS. It is of interest to note that for certain cations (Tl^{+}), during slow filtration of precipitates of hydrogen sulfide group sulfides, coprecipitation is also very greatly evident.

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* Indium can be precipitated as In_2S_3 from 0.08-0.05 N HCl, while Tl_2S and Ga_2S_3 are only deposited from acetic acid solutions.

The percentage coprecipitation of third group cations, as a rule, increases with decreasing solubility of the sulfides of these metals and with decreasing acid content of the solution. The amount of trapped cation also depends on the individual properties of sulfides of both the micro-component and macro-component. The low solubility of the macro-component plays an essential role, as is clearly demonstrated in the case of coprecipitation of indium with HgS. Conditions where both micro- and macro-components are sparingly soluble are particularly favorable for coprecipitation (coprecipitation of In_2S_3 with HgS and CuS).

On considering coprecipitation of cations with various precipitates from the point of view of their capacity to give crystalline modifications, one would expect that the sulfides of individual metals would differ considerably from each other in this connection. The capacity to crystallize is very strongly expressed in the case of CdS, while As_2S_3, even after aging, is amorphous when examined by X-rays. Consequently, the property of various sulfides to coprecipitate cations can be related to their capacity for changing over more or less quickly into a crystalline state, which depends on the polarity of these compounds, and is connected with the position of the element in the periodic table.

Since trapping of Ga^{3+}, In^{3+}, and Tl^{+} occurs during crystallization of HgS, CuS, and CdS particles, there arises the question of the possibility, in the given instances of coprecipitation, of the formation of mixed crystals.

Gallium, mercury, and cadmium sulfides are of the structural type of sphalerite, with the same coordination number 4 and with similar dimensions for the elementary cells (the value of a for Ga_2S_3 is 5.18, for HgS it is 5.84, and for CdS 5.82 A). Furthermore, all these sulfides have a similar type (covalent) of chemical bond.

Thus, thanks to the similarity in the crystallochemical properties of the sulfides being discussed, gallium is trapped by HgS to the extent of 19.9%, while it is trapped to the extent of 12.3% by CdS (after 24 hours aging). It is of interest to note that during aging, the amount of gallium in the HgS precipitate decreases. This phenomenon can be explained on the one hand, by transformation of HgS during recrystallization into another modification of a different structural type and having different values of the elementary cell; moreover, in this case, it is obvious that the ready solubility of Ga_2S_3 in 0.3 N HCl plays an important part.

As for the smaller extent to which gallium is coprecipitated with CdS, this is presumably connected with its greater solubility in hydrochloric acid as compared with the solubility of HgS.

The crystallochemical resemblance between In_2S_3, HgS, and CdS is manifested to a smaller extent. Indium sulfide has a cubic cell, just like mercury sulfide and cadmium sulfide; the dimensions of the elementary cell is equal to 5.36 A and the coordination numbers 4 and 6. Nevertheless, In_2S_3 is of the structural type $\gamma'Al_2O_3$. Thallium sulfide is of structural type CdI_2, and has a laminated lattice, while the value of a is equal to 13.61 A. The amount of thallium coprecipitated with HgS is comparatively small; more is coprecipitated with CdS.

When one compares coprecipitation of cations with sulfides and other analytical precipitates, it is possible to discern many common features. E. g. an increase in coprecipitation during aging of the precipitate in the mother liquor is observed not only for sulfides, but also for other cases (during separation of magnesium and calcium, the latter is precipitated as the oxalate [5]). Purification of precipitate from impurities as a result of recrystallization is known to occur in the case of $BaSO_4$ [6] (separation of Na_2SO_4 on leaving barium sulfate in the mother liquor). This is analogous to what happens during aging of HgS when gallium and thallium go into solution. Coprecipitation of cations with barium sulfate and with cadmium sulfide, in essence, is the same process. In the first instance trapping of cations occurs during growth of the particles found in solution as individual crystals, while in the second trapping of cations is by particles found as aggregates after formation of CdS precipitate.

The relation between the amount of coprecipitated salt and its solubility is demonstrated not only for sulfides but also for other cases. As an example one can quote coprecipitation of barium bromide, chloride, and nitrate with $BaSO_4$, the amount of the salts coprecipitated increasing with decreasing solubility [7].

It follows from our experiments that coprecipitation of cations with sulfides is caused by their recrystallization process during transformation from an amorphous to an ordered crystalline state. Consequently, the division of precipitates into coagulated colloids (sulfides, hydroxides) which have large surfaces, and crystalline (barium sulfate) colloids, and the idea of regarding the mechanism of coprecipitation as being different in the two cases, which follows from this division, cannot be regarded as correct [8].

It is also necessary to point out that coprecipitation of unweighable amounts of materials can also be explained by adsorption processes and by cocrystallization (Khlopin, Gan). In this connection it is natural to assume that in those cases which Khlopin and Gan asign to adsorption, it may actually be a case of coprecipitation caused by crystallization of the precipitates. This is highly probable, because the crystallization process can be completed as rapidly as adsorption.

Alimarin [9] in his paper has shown that division of precipitates into amorphous and crystalline, on the basis of outward morphological signs, and the theory of precipitation founded on this basis have no scientific foundation. In discussing the properties of precipitates the starting point should be the crystalline or amorphous state as established by X-ray analysis.

In developing this idea in relation to the phenomenon of coprecipitation we consider that the process of trapping of cations both by crystalline as well as amorphous precipitates should be considered from the point of view of their crystallization as established by X-ray studies. The existence of a large surface area in the precipitate of coagulated colloids does not appear to be sufficient for coprecipitation.

The part played by the surface in coprecipitation phenomena and which has been clarified in the present investigation, is of essential importance. As our experiments have shown, the existence of a very large surface in the precipitates, together with the HS^- and S^{2-} ions which have a negative charge absorbed on it, does not seem to be a sufficient condition for coprecipitation of third group cations with second group sulfides. The increase or decrease in area on aging does not lead to corresponding changes in the amount of coprecipitated cations. This is also a pointer to the absence of a direct relation between surface area and extent of coprecipitation of impurities, and indicates the effect, in the given case, of other factors. It must be assumed that in a given process the structure of the surface may play a part, while coprecipitation does not occur over the whole surface but only on its active centers.

It is intended in the future to study kinetics of coprecipitation of Ga^{3+}, In^{3+}, and Tl^+ with other sulfides of the hydrogen sulfide group in relation to changes in their structure and surfaces on aging. It is interesting to consider in this respect such sulfides as As_2S_3 prepared in a state which is amorphous according to X-ray study, and which has not been subjected to aging.

In conclusion we should like to thank I. P. Alimarin for directing this work.

SUMMARY

1) The kinetics of coprecipitation of Ga^{3+}, In^{3+}, and Tl^+ with HgS, CuS, and CdS have been studied in connection with aging of these sulfides, and with changes in structure and surface.

2) From microphotographs and experiments on sorption of dyes it follows that during aging of HgS, there occurs a breakdown of particles of this precipitate and a decrease in their size and increase in area, while in the case of CuS the particles aggregate and the area decreases. The effective surface of CdS does not alter on aging.

3) Electronographic study showed that during aging, CuS and CdS recrystallize, their structures become ordered, and crystal size increases. During recrystallization of HgS on the other hand, crystal size decreases.

4) CdS particles which are visible under the electron microscope are aggregates of smaller primary particles which grow during recrystallization. The sizes of particle aggregates does not change during aging.

5) It has been shown that coprecipitation of Ga^{3+} and In^{3+} with CuS and CdS and purification of HgS from Ga^{3+} and Tl^+ are connected with crystallization of HgS, CuS, and CdS, and do not depend on an increase or decrease in the effective surface of the precipitates.

6) During aging of sulfides, coprecipitation may increase (Ga^{3+}, In^{3+} – CuS, CdS), decrease (Ga^{3+}, Tl^+ – – HgS), or remain unchanged (In^{3+} – HgS; Tl^+ – CuS).

7) On the basis of the results obtained some hypotheses are advanced regarding the part played by precipitate surface, and crystallization processes during coprecipitation of cations with sulfides.

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AN INVESTIGATION OF THE FORMATION OF SILVER IODIDE BY THE LIGHT ABSORPTION METHOD

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The use of light absorption as a method for physicochemical analysis has allowed considerable success to be achieved in the theory of photometric methods; in particular, the mechanism of many reactions which occur in a homogenous medium has been studied. Thus, I. V. Tananaev [1, 2], has studied the formation of silicomolybdic acid in iodoplatinate. A. K. Babko and coworkers have studied interation between metal ions and various organic compounds, e.g. interactions between zinc, cadmium, and lead respectively, with dithizone [3], mercury with pinacyanol [4], iron with pyrocatechol [5], copper with salicylate and pyridine [6], the thiocyanate complexes of metals [7], etc.

Hitherto, turbidimetry has only been developed to a small extent from a theoretical viewpoint. Most of the work carried out on turbidimetry is of a practical nature. A number of investigations have been devoted to barium sulfate, chosen as an object for study in order to try and establish the general rules of turbidimetry. Here mention may be made of the thorough work of Ringbom [8]. Formation of $BaSO_4$ was first used by Campo [9], and Chepelevetsky [10], for titration according to maximum turbidity. Lure and Tal [11, 12] have established optimum conditions for turbidimetric determination of lead, zinc, chlorides, and copper. Bobtelsky [13] has published a number of papers on phototurbidimetric titration in recent years.

I. V. Tananaev and coworkers have used light absorption as a measurable property in physicochemical analysis during the study of reaction mechanisms in heterogeneous media. Thus, I. V. Tananaev and M. I. Levina [14] have made a study of the system $CoSO_4$ $[K_4Fe(CN)_6] - H_2O$, during which it was established that formation of a mixed ferrocyanide of cobalt and potassium with the formula $5Co_2Fe(CN)_6 IK_4[Fe(CN)_6]$ occurs, the individuality of this compound being established by another method. The following systems were also studied: $K_2PdCl_4-KI-H_2O$ [15], $BaSO_4-BaCl_2-C_2H_5OH-H_2O$ [16], $BaSO_4-NaCl-C_2H_5OH-H_2O$ [17], and others.

An important part is played in turbidimetry by the degree of dispersion of the solid phase, dispersion being dependent on many factors. The relation between light absorption and the dispersion of the solid phase during precipitation is expressed by a curve with a maximum, while the minimum value of light absorption corresponds to both the lowest as well as to the highest percentage dispersion of the solid phase. In this connection it may be assumed that e.g., an increase in solubility – with its attendant increase in particle size – should lead to an increase or decrease in light absorption according to how the given point is located relative to the maximum on the light absorption - degree of dispersion curve.

The aim of the work described here was to obtain, on the basis of physicochemical analysis, new data relating to the study of the laws of light absorption of suspensions during their formation, and to accumulate data on the relation between their solubility and light absorption.

Silver halides were chosen as subjects for study on the grounds that although similar in composition, they differ in solubility. Moreover, the simplicity of the composition of silver halide precipitates reduces the number of complications which usually develop when working with ions of higher valency.

EXPERIMENTAL PROCEDURE

Experiments were carried out while one component was kept at a constant concentration while the other was varied, as well as under conditions where the total concentration of both components was kept constant while the ratio of one component to the other was varied (the method of isomolar series).

Suitable suspensions were prepared and their light absorption measured as follows: into a cell placed in the appropriate receptacle in an electrophotocolorimeter, specially adapted for turbidimetric determinations (A. L. Davydov system) was poured a solution of potassium halide in sufficient amount to give the required concentration, this was followed by water so that the final volume was 50 ml; finally the appropriate amount of silver nitrate was added while the solution was stirred at a constant rate by means of a motor. In those cases where other components were to be added in order to alter the solubility of the solid phase, or where a stabilizing agent was to be added, addition was carried out before the precipitant was added.

On the basis of the results obtained diagrams of composition against extinction were plotted.

The System $AgNO_3 - KI - H_2O$ (Determination of the Composition of the Precipitate)

During study of this system measurements were made of the light absorption of mixtures of silver nitrate and potassium iodide, in which the sum of the molar concentrations of the latter was constant and amounted to 8×10^{-3} mole/liter; the value of the ratio KI:$AgNO_3$ was varied within the limits 0.2 to 3. As can be seen from the results which are given in Table 1 and Fig. 1, the light absorption maximum is located on the composition ordinate and corresponds to a ratio of KI:$AgNO_3$ of 1. The shape of the maximum (the long peak) testifies to a strong change in the degree of dispersion in the region adjoining the stoichiometric ratio of the components.

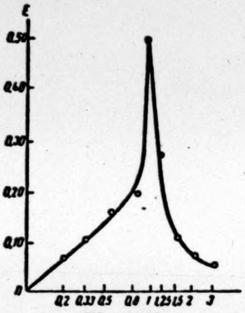

Fig. 1. Change in extinction in the system $AgNO_3 - KI - H_2O$. $\Sigma AgNO$, $AgNO_3 + KI = 8 \cdot 10^{-3}$ mole/liter.

TABLE 1

Extinction in the System $AgNO_3 - KI - H_2O$.
$AgNO_3 + KI = 8 \cdot 10^{-3}$ mole/liter

$\frac{KI}{AgNO_3}$	Galvanometer reading	Extinction ε	Molar extinction coefficient
0.2	85	0.07	19.8
0.33	80	0.10	19.0
0.5	69	0.16	22.6
0.8	68	0.19	18.2
1.0	32	0.50	47.0
1.25	53	0.28	29.6
1.5	77	0.11	12.9
2.0	83	0.08	11.3
3.0	87	0.06	11.3

The results obtained show that by studying a heterogeneous system by the light absorption method, it is possible to establish the composition of a precipitate even in those cases where the degree of dispersion of the latter changes rapidly.

The System $AgI - KI - H_2O$ [*]

This system was studied with the aim of establishing the influence shown on the light absorption of AgI suspensions by I ions, the solubilizing action of which at high concentrations relative to AgI (as a result of complex formation) is well known.

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[*] According to actual experimental conditions, the given system belongs to the four component systems and should be written $AgNO_3 - KI - H_2O$. But, since the concentration of $AgNO_3$ in all mixtures was a constant, and, furthermore, is very small in comparison with KI concentration, which is 500 times as much, the system can be regarded as a three-component one: $AgI - KI - H_2O$ (a system of two salts with a common ion). The concentration of the KNO_3 formed during the exchange reaction is very small and can be neglected. This was demonstrated experimentally in the system $AgBr - KNO_3 - H_2O$, which did not show appreciable changes in light absorption on changing KNO_3 concentration within wide limits.

In this system the concentration of $AgNO_3$ was constant (10^{-3} mole/liter); the amount of KI, which was in excess of the stoichiometric amount, was varied from 10^{-3} to 5×10^{-1} mole/liter. Results of measurements of the light absorption of mixtures are given in Table 2 and in Fig. 2.

TABLE 2

Change in Extinction in the System AgI – – KI – H_2O (constant concentration of AgI = 1×10^{-3} mole/liter)

[KI] in excess, mole/liter	– log [KI], excess	Galvanometer reading	Extinction	Molar extinction coefficient
10^{-3}	3	97	0.01	3.8
10^{-2}	2	97	0.01	3.8
10^{-1}	1	89	0.06	18.9
$2 \cdot 10^{-1}$	0.7	31	0.51	192.0
$3 \cdot 10^{-1}$	0.5	44	0.36	136.0
$4 \cdot 10^{-1}$	0.4	64	0.19	71.6
$5 \cdot 10^{-1}$	0.3	0	0	0

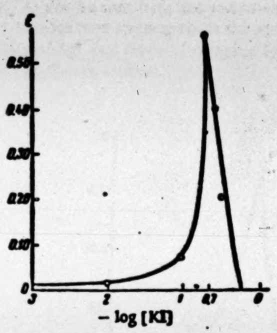

Fig. 2. Change in extinction in the system AgI – KI – H_2O: [AgI] = 1×10^{-3} mole/liter.

As the curve shows, light absorption remains practically constant in the concentration range KI = 10^{-3} to 10^{-1} mole/liter. Starting at 10^{-1} mole/liter of KI, light absorption increases rapidly and attains a maximum value at 2×10^{-1} mole/liter; on increasing the concentration further light absorption drops and becomes zero at roughly 5×10^{-1} mole/liter.

The small change in light absorption for a definite concentration range of potassium iodide can be explained by the mutually balancing effect of two counteracting factors – common ion effect which depresses precipitate solubility, and the dissolving action of the same ions linked with complex formation; as a consequence of these two factors, the amount of precipitate and its degree of dispersion remain unchanged. On increasing KI concentration further, the solubility of AgI increases so much that it leads to an increase in particle size with a consequent sharp increase in light absorption. At even higher KI concentrations, the solubility of AgI continues to increase, leading to an appreciable drop in the amount of precipitate; this, together with the increasing particle size, leads finally to a sharp decrease in light absorption.

The increase in light absorption of AgI suspensions which results to a certain extent from an increase in its solubility is a consequence of the fact that AgI, in natural conditions of precipitation, separates out in a highly dispersed state which determines its position to the right of the maximum on the curve for degree of dispersion – light absorption.

The extent of the increase in the extinction of AgI suspensions for a certain increase in its solubility is clear from the following comparison: the concentration of the solid phase in the given system is practically the same – 10^{-3} mole/liter (in each case up to the maximum on the curve), while in the absence of excess KI, and at a concentration of the latter of 0.2 mole/liter, extinction has the following respective values: 0.02 and 0.51. This is also clear on comparing experimental results with results of the previous system, in which maximum extinction (0.50) was observed for an AgI precipitate obtained at a stoichiometric ratio of $AgNO_3$ and KI; under these conditions however, the concentration of $AgNO_3$ and KI was four times as much.

The maximum value of the molar extinction coefficient obtained for this system was 192. But, as is evident from other systems containing AgI, which we have studied, this value is not the highest possible.

The System AgI – $AgNO_3$ – H_2O

This system was examined in order to establish the effect of excess Ag^+ ions on the light absorption of AgI suspensions. For this purpose measurements were made of the light absorption of mixtures in which the content of KI was constant (1×10^{-3} mole/liter), while the excess (greater than the stoichiometric value) concentration of $AgNO_3$ was varied from 1×10^{-3} to 5×10^{-1} mole/liter. As can be seen from the results obtained (Table 3, Fig. 3) a certain excess of Ag^+ ions just like an excess of I^- ions leads to an increase in the extinction of AgI. This fact must also be ascribed to an increase in the solubility of AgI as a result of complex formation. It is obvious in this instance that cationic complexes of the type $[Ag_2I]^+$ are formed.

TABLE 3

Change in Extinction in the System AgI–$AgNO_3$–H_2O (constant concentration of AgI = 1×10^{-3} mole/liter).

$[AgNO_3]_{excess}$, mole/liter	– log. $[AgNO_3]_{ex}$	Galv. reading	Extinction
10^{-3}	3	97	0.01
10^{-2}	2	97	0.01
$5 \cdot 10^{-2}$	1.3	81	0.10
$1 \cdot 10^{-1}$	1	66	0.18
$2 \cdot 10^{-1}$	0.7	48	0.32
$5 \cdot 10^{-1}$	0.3	0	0

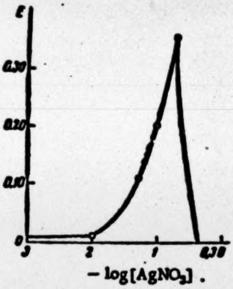

Fig. 3. Change in extinction in the system AgI – $AgNO_3$ – H_2O; [AgI] = $1 \cdot 10^{-3}$ mole/liter.

The System AgI – NH_3 – H_2O

This system was studied in order to get confirmation for the hypothesis advanced above, that the increase in light absorption of a suspension of AgI when there is present a certain excess of I^- or Ag^+ ions, is caused by an increase in solubility consequent upon complex formation. If this hypothesis is correct then other solvents, in particular ammonia, should behave similarly. Ammonia is a relatively weak complexing agent for Ag^+ ions, but, it may be expected that at large concentrations of ammonia, it might be possible to increase the solubility of AgI suspensions to the level necessary for an increase in particle size and to an increase in light absorption.

TABLE 4

Change in Extinction in the System AgI – NH_3 – H_2O (constant concentration of AgI = 1×10^{-3} mole/liter)

NH_3, mole/liter	Galvanometer reading	Extinction	Molar extinction coefficient
0.5	30	0.52	196
1	27	0.57	215
2	22	0.66	248
3	23	0.64	242
4	28	0.55	208

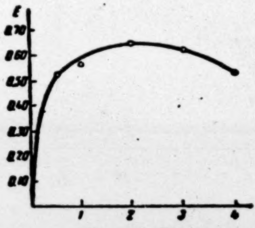

Fig. 4. Change in extinction in the system AgI – NH_3 – H_2O; [AgI] = 1×10^{-3} mole/liter.

With this idea in mind we measured the light absorption of mixtures containing equivalent amounts of $AgNO_3$ and KI necessary for obtaining 1×10^{-3} mole/liter; the amount of ammonia was varied.

As the results obtained show (Table 4, Fig. 4), when ammonia is present in the system, in accordance with the hypothesis advanced above, there is an appreciable increase in light absorption of AgI suspensions; under such conditions, there is a particularly sharp increase in extinction at a relatively low ammonia content. At a NH_3 concentration of 0.5 mole/liter light absorption becomes 0.52. Maximum light absorption is observed for a content of ammonia of about 2 moles/liter. Increasing the NH_3 concentration beyond 2 moles/liter does not have any essential effect on light absorption.

Of the systems containing AgI which we have described, it was only in this system that the highest value for the molar extinction coefficient was achieved (248). In this connection, differences in the values of the latter are not completely understood in the systems $AgI - KI - H_2O$ and $AgI - NH_3 - H_2O$. If one assumes that the maximum light absorption can be established by studying the function extinction – suspension solubility, then this point should be repeated in both of these systems. This is not observed in practice. The difference is so considerable (248 and 192) that it compels one to advance the theory that the solid phase (AgI) which separates out in both cases, is different in character.

The System $AgI - AgNO_3 - NH_3 - H_2O$

This system was studied with the aim of establishing the nature of the effect of excess Ag^+ ions on the behavior of AgI suspensions in the presence of ammonia. Under such conditions the solubility of AgI in ammonia should decrease; this in turn should affect the rate at which precipitate separates out, and, consequently, on the extent to which it is dispersed and on the light absorption associated with this.

We measured extinction for a series of mixtures containing 10^{-3} mole/liter of KI, and $AgNO_3$ in an amount necessary for giving an excess of 4×10^{-3} mole/liter; the amount of ammonia was varied within the limits 1 to 4 moles/liter.

It is evident from the results obtained (Table 5, Fig. 5), that a sharp increase in extinction is obtained at a higher ammonia concentration than in the system $AgI - NH_3 - H_2O$, i.e. 2 moles/liter instead of 0.5. For the same ammonia concentration of 1 mole/liter, extinction for 10^{-3} mole/liter of AgI in the absence of excess silver nitrate is 0.57, while for a concentration of the latter of 4×10^{-3} mole/liter, the extinction is 0.10. When the ammonia concentration is 2 moles/liter, the value of the extinction is the same both in the presence of excess $AgNO_3$ and in the absence of the latter. It is obvious that for this concentration of ammonia, the concentration of silver ions complexed as an ammonia complex decreases so much, that it shows no further influence on the solubility of the AgI.

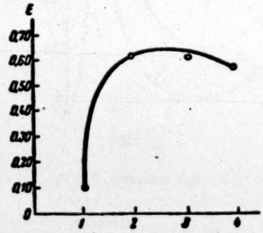

Fig. 5. Change in extinction in the System $AgI - AgNO_3 - NH_3 - H_2O$. $[AgI] = 1 \times 10^{-3}$ mole/liter; $[AgNO_3]$ excess $= 4 \times 10^{-3}$ mole/liter.

TABLE 5

Change in Extinction in the System $AgI-AgNO_3-NH_3-H_2O$. $[AgI] = 1 \times 10^{-3}$ mole/liter; $[AgNO_3]$ excess $= 4 \times 10^{-3}$ mole/liter

NH_3, mole/liter	Galvanometer reading	Extinction	Molar extinction coefficient
1	79	0.10	37.8
2	24	0.62	234.0
3	25	0.60	226.0
4	26	0.59	222.0

The experimental results obtained confirm the correctness of our assumption regarding the presence of a regular relation between the degree of dispersion of the precipitate (and consequently, its light-absorption) and its solubility. This is graphically demonstrated by comparing the general diagram for light absorption - composition, in which is represented the effect on AgI of excess of both I^- anions as well as Ag^+ cations, with the diagram of solubility in a common system.

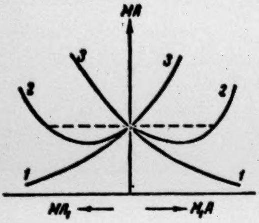

Fig. 6. Solubility of salt (MA) in the presence of electrolytes with common ions (M_1A and MA_1).

The article of Tananaev, Mizetskkaya, and Vinogradowa [18] includes a classification of systems of precipitates based on the results of the solubility of the latter in the presence of excess common ions, both cations and anions. On the open diagram for various types of solubility curves proposed by the authors indicated, (Fig. 6, Curve 2 - 2), the systems which we have been studying would be characterized as systems with partial two-sided salting out of the precipitate (lowering of solubility) with subsequent complex formation (increase of solubility) because of the common ion effect – anions as well as cations.

In Fig. 7. are given two diagrams: 1) a diagram of light absorption – composition, in which is shown the effect of Ag^+ as well as I^- ions on the extinction of AgI suspensions, and 2) a diagram of solubility in a common ion system. As these diagrams show, there is a definite onnection between solution processes and light absorption of suspensions.

In this connection it would be possible to speak of a correlation of the diagram of properties, supplemented y the method of suspension extinction. This question deserves attention from the point of view of the methods f physicochemical analysis.

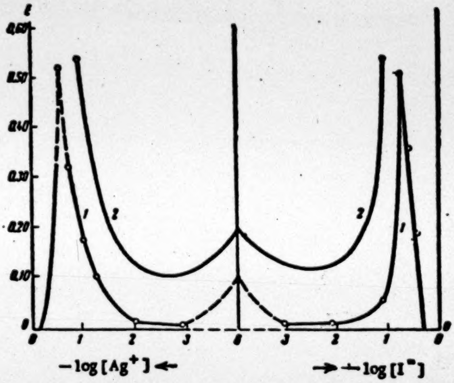

Fig. 7. Systems $AgI - Ag^+ - H_2O$ and $AgI - I^- - H_2O$: Curve 1) composition – extinction; Curve 2) composition – – solubility.

Phototurbidimetric Determination of Iodine by a Calibration Curve Method

By studying the systems $AgI - NH_3 - H_2O$ and $AgI - AgNO_3 - NH_3 - H_2O$ it was established that it is possible to increase the light absorption of AgI suspensions considerably by adding ammonia, while by carrying out measurements in the presence of a certain excess of $AgNO_3$ it is possible to preserve the zone of maximum light absorption over a fair range (2 - 4 moles/liter). On the basis of these results an attempt was made to carry out a phototurbidimetric determination of small amounts of I^- ions by a calibration curve method.

For this purpose various amounts of KI in successively increasing quantities were introduced into the colorimeter cell followed by a constant amount of ammonia, so that its amount in the final volume (50 ml) was 4 moles/liter; next, using a stirrer; $AgNO_3$ was added in an amount sufficient to give an excess concentration of 4×10^{-3} mole/liter.

TABLE 6

Results for the Calibration Curve

I^-, gram ions/liter	Galvanometer reading	Extinction
$1 \cdot 10^{-6}$	87	0.08
$2 \cdot 10^{-6}$	76	0.12
$3 \cdot 10^{-6}$	65	0.19
$4 \cdot 10^{-6}$	56	0.25
$5 \cdot 10^{-6}$	49	0.31
$6 \cdot 10^{-6}$	42	0.38
$7 \cdot 10^{-6}$	38	0.42
$8 \cdot 10^{-6}$	36	0.45
$9 \cdot 10^{-6}$	32	0.49

TABLE 7

Results for Phototurbidimetric Determination of I

I^-, gram ions/liter		Error in %
taken	found	
$2 \cdot 10^{-6}$	$2 \cdot 10^{-6}$	0.0
$4 \cdot 10^{-6}$	$4.1 \cdot 10^{-6}$	+2.5
$7 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$	−2.9
$9 \cdot 10^{-6}$	$9.32 \cdot 10^{6}-$	+3.6

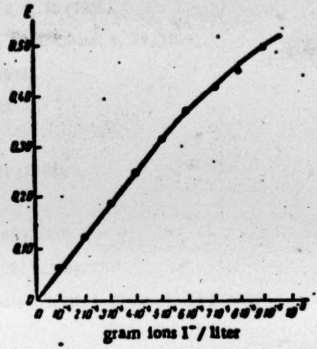

Fig. 8. Calibration curve for phototurbidimetric determination of iodine ions.

Results of measurements of the extinction were used for constructing a calibration curve (Table 6, Fig. 8.). Table 7 contains the results obtained during analysis of samples with an unknown content of I^- ions.

It has thus been demonstrated in principle that it is possible to increase the sensitivity of the phototurbidimetric method of determination by changing (in the given instance, increasing it) the solubility of the solid phase.

SUMMARY

The heterogenous systems $AgNO_3 - KI - H_2O$; $AgI - KI - H_2O$; $AgI - AgNO_3 - H_2O$; $AgI - NH_3 - H_2O$; and $AgI - AgNO_3 - NH_3 - H_2O$ have been studied by the method of measuring light extinction on the basis of a physicochemical technique of analysis. It has been demonstrated that the composition of the precipitate can be established from the position of the maximum on the diagram composition – property, despite the polydispersed state of the solid phase.

It has been established that there is an interconnection between the light absorption of silver iodide and its solubility, and consequently, its degree of dispersion. It has been shown that a certain increase in the solubility of AgI can be used for increasing the sensitivity of phototurbidimetric determination.

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URANYL AND THORIUM SELENITES

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Berzelius [1] was the first to prepare uranyl selenite. Nilson [2] and Boutzoureano [3], while studying the interaction of UO_2^{2+} ions with a concentrated solution of sodium selenite, found that the lemon-yellow precipitate formed on adding together the original materials, at room temperature, corresponds in composition to the formula $UO_2SeO_3 \cdot 2H_2O$. Anhydrous uranyl selenite has been prepared as yellow prismatic crystals by heating a mixture of uranyl selenite dihydrate with a solution of selenious acid in a sealed tube [3]. This compound is practically insoluble in water but readily dissolves in dilute acids. Anhydrous uranyl selenite is stable at 100°, but decomposed at higher temperatures with liberation of selenium dioxide to form uranoso uranic oxide.

An amorphous precipitate of thorium selenite $Th(SeO_3)_2 \cdot H_2O$ was obtained by Cleve [4], on pouring together solutions of thorium chloride and selenious acid. There are references to the fact that during slow addition of a solution of thorium sulfate to a concentrated solution of sodium selenite, there separates a flocculent precipitate of the octohydrate $Th(SeO_3)_2 \cdot 8H_2O$ [2]. After long contact between precipitate and mother liquor there appear obvious signs of a crystalline structure. This salt is practically insoluble in water but readily dissolves in mineral acids.

Selenious acid has been used for determining thorium, and also for separating it from beryllium and a number of other cations [5]. According to Deschmukh and Swamy [6], thorium selenite is precipitated in the pH range 5.5. – 6; experimental error does not exceed 1%.

Dzhoshi [7] found recently that uranium is quantitatively precipitated by selenious acid from uranyl salt solutions in 50% alcohol at a pH of 4 - 5.

In the work described here, a study was made of the conditions for precipitating uranyl and thorium selenites from their solutions in nitric and sulfuric acids; in addition, their solubility in dilute solutions of these acids was determined, and their solubility products calculated.

EXPERIMENTAL

Uranyl and thorium selenites were synthesized from chemically pure reagents. Selenious acid and its salts were prepared according to published results [8].

The quantitative determination of selenium, uranium, and thorium was taken from Gillebrand and Lendel's textbook [9].

Uranyl Selenite. On mixing equal volumes of 1 N solutions of $UO_2(CH_3COO)_2$ and H_2SeO_3, preliminarily warmed to 50°, a yellow precipitate separated out which was aged for several days in the mother liquor in a thermostat kept at 50°; the mother liquor was decanted off, and the precipitate washed and dried at 100°, and finally analyzed. Uranium was determined gravimetrically as uranoso uranic oxide after removal of selenium. SeO_3^{2-} was reduced with hydrazine and weighed as elemental selenium. Analysis of this precipitate showed that it did not contain water, while the ratio of the number of uranium atoms to the number of selenium atoms was within the limits 1:1.02 to 1:1.05; this corresponds to the formula UO_2SeO_3.

In order to study the composition of the precipitate at various stages of the precipitation process, various amounts of a standard solution of H_2SeO_3 was added with stirring to equal aliquots of a standard solution of

$UO_2(CH_3COO)_2^{2-}$. After precipitation of uranyl selenite, the residual amount of UO_2^{2+} was determined in solution. Analytical results are presented graphically on Fig. 1 a. The path taken by straight line a allows one to conclude that during the precipitation process, the composition of the precipitate always corresponds to the formula indicated.

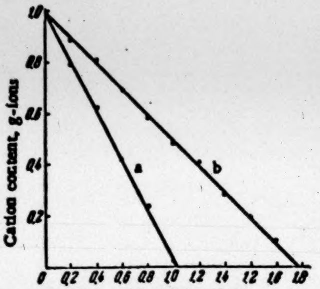

Fig. 1. Change in cation content in solution during precipitate formation:
a) uranyl selenite; b) thorium selenite.

Thorium Selenite. To a 1 N thorium chloride solution heatead to 50° was added, with stirring, a concentrated solution of selenious acid taken in 25% excess of the stoichiometric proportion. The precipitate of thorium selenite was kept in the mother liquor for several days, after which the mother liquor was decanted off, the precipitate was washed until it gave no further reaction for chloride ions, when it was dried at 100° and analyzed. Thorium was determined gravimetrically as the dioxide, while selenium was determined in the same way as indicated for uranyl selenite. Thorium selenite was found to contain no water, while the ratio of the numbers of thorium and selenium atoms was found to be 1:1.98.

A study of the composition of thorium selenite during precipitation showed that in this case there are only insignificant deviations from this ratio (Fig. 1 b).

A Study of the Precipitation of Uranyl and Thorium Selenites. The pH at which the selenites were precipitated was measured with a glass electrode on a pH meter made in the Ural Scientific Research Institute of Chemical Machine Construction Factory. The accuracy of measurement was ± 0,05 pH units. The operation of the pH meter was checked with standard buffer solutions prepared according to Britton [10]. The exact value of the pH of buffer solutions was established potentiometrically by means of a quinhydrone electrode. Nitric and sulfuric acid solutions of uranyl and thorium of different concentrations with respect to the metals were prepared. The solutions contained the respective acids in concentrations of 30 g/liter. Sodium selenite 20% in excess of the stoichiometric amount was added to the acidified solutions. No precipitates were formed at this acidity. The beaker containing the solution was placed on a rotating stand and a glass electrode immersed in the liquid. The acidity was lowered by gradual addition of 8% ammonia solution with vigorous stirring. The moment at which an opalescence appeared, this being readily observable by side illumination of the beaker, was taken as the beginning of precipitation and was denoted by $pH^{b.p.}$; completion of precipitation was designated by $pH^{c.p.}$ and was fixed on the basis of a negative reaction for uranium in the filtrate (from the beaker). During precipitation of thorium selenite, qualitative reactions proved to be insufficiently sensitive, and completion of precipitation was determined as that point when thorium could not be detected in the liquid phase by quantitative methods of analysis. Experiments were carried out at 22°. The results obtained are given in Tables 1 and 2.

TABLE 1

pH Values during Precipitation of Uranyl Selenite (mean of three and more replicates)

Medium	Uranium conc, g/liter	$pH^{b.p.}$	$pH^{c.p.}$
Nitric acid	0.5	2.25	3.15
	1.0	1.90	2.60
	2.0	1.58	2.40
	3.0	1.47	2.30
Sulfuric acid	0.5	3.40	4.10
	1.0	3.10	3.80
	2.0	2.65	3.30
	3.0	2.40	3.10

TABLE 2

pH Values during Precipitation of Thorium Selenite (mean of three and more replicates)

Medium	Thorium conc. g/liter	$pH^{b.p.}$	$pH^{c.p.}$
Nitric acid	0.5	1.20	1.65
	1,0	1.00	1.40
	2.0	0.87	1.15
	3.0	0.75	1.06
Sulfuric acid	0.5	2.47	3.20
	1.0	2.05	2.90
	2.0	1.75	2.64
	3.0	1.60	2,47

With increasing cation concentration, uranyl and thorium selenites were precipitated from more acid solution. In sulfuric acid solutions, precipitation was displaced towards higher pH values than in nitric acid solutions. In another series of experiments precipitation was studied during gradual change in pH in the precipitation range. In the pH range at which precipitation of uranyl and thorium selenites occurred, the acidity was lowered stepwise at the rate of a tenth of a pH unit. Solution plus precipitate were kept at the new pH value for 10 - 15 minutes; liquid and solid phases were then separated by centrifuging. Uranium and thorium respectively were determined in the solid phase gravimetrically, while the liquid phase was subjected to a further change in pH and this process repeated until precipitation was complete. The excess of selenite used was 20% greater than the stoichiometric amount. Temperature was kept constant at 20°. The initial concentration of uranium and thorium was 3 g/liter. The results obtained are shown graphically on Fig. 2.

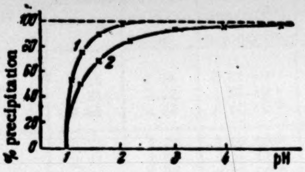

Fig. 2. Precipitation of uranyl and thorium selenites (in %) during stepwise change in pH
1) uranyl selenite; 2) thorium selenite

The amount of precipitated metal expressed as a percentage of the amount of metal originally taken is plotted along the ordinate. The corresponding pH changes are plotted along the abscissa. It is clear from the curves that precipitation of the selenites, in the main, proceeds during insignificant changes in pH from the moment when precipitation starts. For complete precipitation of uranyl and thorium selenites a considerably greater drop in acidity is required – as a result of this, the precipitation range is extended. Large excess of precipitant leads to a cutting down of the precipitation range; precipitation occurs at lower pH values.

Solubility and Solubility Products of Uranyl and Thorium Selenites. The solubility of these selenites was studied in dilute nitric and sulfuric acid solutions. pH was was measured on a MOSKIP pH-meter. Accuracy of pH measurement was ±0.01 pH units. Saturated solutions were prepared by placing flasks containing uranyl (thorium) selenite and an acid solution of known pH in a thermostat. Temperature was kept constant to an accuracy of 0.05°. It was found that shaking the flasks for 8 hours was sufficient to reach equilibrium. The composition of the solid phase did not change during preparation of saturated solutions. pH was measured in one aliquot of saturated solution, while in another aliquot the concentration of metal ion was determined in the liquid phase by quantitative analysis. Uranium was determined by means of an FEK-M photocolorimeter. Solubility product was calculated by means of the formulas proposed by Babko for precipitates soluble in acids [11]. This method has been used by Korenman for finding the solubility product of the oxalates of a number of rare earth elements [12]; the method of calculation was checked by him during determination of the solubility product of calcium oxalate and was shown to yield good results. Earlier, this method had been used by Zharovsky for determining the solubility product of phosphates [13]. The concentration of selenite ions required for calculation of the solubility product was determined from the value of the dissociation constant of selenious acid, and the hydrogen ion concentration. Dissociation of selenious acid has been studied by many investigators [14 - 19]. Britton and Robinson found $K_1 = 2.88 \times 10^{-3}$ and $K_2 = 0.95 \times 10^{-8}$ by the method of potentiometric titration with a glass electrode at 18° [17]. Using potentiometric titration with a quinhydrone electrode, German, Britton, and Robinson [18], found $K_1 = 3.09 \times 10^{-3}$ and $K_2 = 0.89 \times 10^{-8}$ at 17°. Willcox and Prudeaux [19], also using a potentiometric method found $K_1 = 4. \times 10^{-3}$ and $K_2 = 0.87 \times 10^{-8}$ at room temperature [19].

In the present instance we used the values found by Rumpf [15]; using a potentiometric method and a glass electrode, he found that at 20° $K_1 = 4 \times 10^{-3}$ and $K_2 = 1 \times 10^{-8}$. The total concentration (S) of acid with the same ion as the precipitate is given by:

$$[S] = [H_2SeO_3] + [HSeO_3^-] + [SeO_3^{2-}].$$

It was found from the concentration of the metal ion in the saturated solution. For uranyl selenite $[S] = [UO_2^{2+}]$; for thorium selenite $[S] = 2\,[Th^{4+}]$.

Results for calculations of the solubility product of uranyl and thorium selenites are given in Tables 3 and 4.

TABLE 3

Solubility and Solubility Product of Uranyl Selenite (T = 20°) (Mean of two and more replicates)

Solution	pH before shaking	pH of saturated solution	Concentration $[UO_2^{2+}]$, g-ions/liter	$p[UO_2^{2+}]$	pq	$p[SeO_3^{2-}]$	$p[UO_2^{2+}][SeO_3^{2-}]$*
Sulfuric acid	2.38	2.58	$3.81 \cdot 10^{-3}$	2.47	5.65	8.07	10.49
	2.75	3.12	$1.67 \cdot 10^{-3}$	2.78	4.97	7.75	10.53
	2.06	2.32	$6.12 \cdot 10^{-3}$	2.21	6.06	7.79	10.48
Nitric acid	2.72	3.17	$2.09 \cdot 10^{-3}$	2.68	4.91	7.59	10.27
	2.41	2.69	$4.21 \cdot 10^{-3}$	2.38	5.50	7.88	10.26
	1.98	2.29	$6.85 \cdot 10^{-3}$	2.17	6.08	8.25	10.42

* Mean value $[UO_2^{2+}][SeO_3^{2-}]$ ... $3.80 \cdot 10^{-11}$.

TABLE 4

Solubility and Solubility Product of Thorium Selenite (T = 20°) (Mean of two and more replicates)

Solution	pH before shaking	pH of saturated solution	Concentration $[Th^{4+}]$, g-ions/liter	$p[Th^{4+}]$	pq	$p[SeO_3^{2-}]$	$p[Th^{4+}][SeO_3^{2-}]$*
Sulfuric acid	2.69	4.25	$7.12 \cdot 10^{-5}$	4.15	3.75	7.80	19.35
	2.06	2.58	$7.46 \cdot 10^{-4}$	3.13	5.55	8.38	19.89
	1.81	2.17	$1.38 \cdot 10^{-3}$	2.86	6.44	9.00	20.86
Nitric acid	2.88	4.60	$4.37 \cdot 10^{-5}$	4.36	3.40	7.46	19.28
	2.30	3.16	$3.73 \cdot 10^{-4}$	3.43	4.91	8.04	19.51
	1.98	2.43	$8.47 \cdot 10^{-4}$	3.07	5.85	8.62	20.31

* Mean value $[Th^{4+}][SeO_3^{2-}]^2$ ... $1.35 \cdot 10^{-20}$.

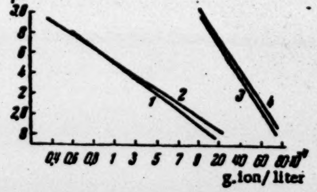

Fig. 3. Solubility of uranyl and thorium selenites in dilute nitric and sulfuric acid solutions 1) Thorium selenite – sulfuric acid; 2) Thorium selenite – nitric acid; 3) Uranyl selenite – sulfuric acid; 4) Uranyl selenite – nitric acid.

On the basis of the values found for the solubility, the curves shown on Fig. 3 were constructed.

If the concentration of metal ion in solution is equal to the total concentration of selenious acid, then according to these curves, it should be possible to find the value of the solubility of the selenite for various values of the pH of the solution above the precipitate. E. g. at a pH of 2.5, for the solution above a precipitate of uranyl selenite, the solubility is equal to 3.2×10^{-3} g. ions/liter.

The curves enable one to determine the value of the pH at which the precipitate can be regarded as practically insoluble ($[Me^{n+}] = 10^{-6}$ g. ions/liter) as long as there is no excess precipitant ions in solution.

SUMMARY

1) The pH range has been found for precipitation of uranyl and thorium selenites from sulfuric and nitric acid solutions.

2) Solubility products have been calculated on the basis of the solubility of the selenites in these acids:

Uranyl selenite $[UO_2^{2+}][SeO_3^{2-}]$ ... $3.8 \cdot 10^{-11}$.

Thorium selenite $[Th^{4+}][SeO_3^{2-}]^2$... $1.35 \cdot 10^{-20}$.

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CHEMICO-ANALYTICAL PROPERTIES OF XANTHOGENATES

4. SOLUBILITY PRODUCTS OF ZINC, NICKEL, IRON, AND CADMIUM XANTHOGENATES

A. T. Pilipenko, T. P. Varchenko, E. S. Kudelya, and A. P. Kostyshina

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In our first article we established the solubility product of silver xanthogenate [1], and gave the solubility series of a number of metallic ethylxanthogenates.

In the present article we give the results of experimental determinations of the solubility products of the methyl-, ethyl-, and butyl-xanthogenates of zinc, nickel, cadmium, of iron ethylxanthogenate, and of nickel propylxanthogenate.*

In order to determine the solubility product of heavy metal xanthogenates, we used the method of determining the solubility in water and in solutions of complexing agents. Heavy metal xanthogenates were prepared by the action of excess potassium xanthogenate on solutions of the respective metal salt, followed by careful washing of the precipitate with water. Saturated solutions of heavy metal xanthogenates in water, and in solutions of various strengths of complexing agents, were obtained by shaking the solid xanthogenate with water or solution respectively. After a definite time interval a sample was taken and its metal content determined. When two successive samples gave identical results, saturation was regarded as complete and the sample was finally analyzed in several replicate determinations. The mean value of the results obtained was taken and the solubility product of the xanthogenate of the particular metal under test determined.

Zinc Xanthogenates

Into two flasks with ground stoppers were placed aliquots of the appropriate zinc xanthogenate, and distilled water added; the whole was then shaken on a mechanical shaker. After 1, 3, and 6 hours, the flasks were placed in a thermostat operating at 20°; three samples were taken from each flask, and zinc content determined by titration of the solution with $K_4Fe(CN)_6$ in the presence of $K_3Fe(CN)_6$ and diphenylamine; it was also determined photometrically by the dithizonate method, and polarographically. The following results were obtained by these methods:

$$L_{s\ \mathrm{Zn(CH_3OCS_2)_2}} = (2.85 \pm 0.5) \cdot 10^{-8};\quad L_{s\ \mathrm{Zn(C_2H_5OCS_2)_2}} = (1.31 \pm 0.2) \cdot 10^{-8};$$
$$L_{s\ \mathrm{Zn(C_4H_9OCS_2)_2}} = (3.76 \pm 0.91) \cdot 10^{-9}.$$

Thus, the solubility of the zinc xanthogenates decreases with increasing molecular weight of the xanthogenate radical.

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* A year after submitting this article to the editor, a paper by I. A. Kakovsky was published (Collection of Papers of the Institute of Mining Acad. Sci. USSR, III, 1956, p. 255) in which the activity products of the xanthogenates of many heavy metals were given. Although we cannot discuss this work here, nevertheless we thought that we should bring readers' attention to it.

Cadmium and Nickel Xanthogenates

The following equilibrium processes were studied as a preliminary to determining the solubility product of cadmium and nickel xanthogenates*:

$$\mathrm{CdX_2 + 4NH_3 \rightleftarrows [Cd(NH_3)_4]^{2+} + 2X^-}$$
$$\mathrm{NiX_2 + 4NH_3 \rightleftarrows [Ni(NH_3)_4]^{2+} + 2X^-}. \qquad (1)$$

The technique was the same as that used for studying the solubility of zinc xanthogenates, except that here aqueous solutions of ammonia of varying concentration were used instead of water. Cadmium was determined photometrically by the dithizonate method, gravimetically as $\mathrm{CdSO_4}$, and polarographically. Nickel was determined gravimetrically and photometrically as the dimethylglyoximate.

Equations used for calculation were derived on the following assumptions. In a saturated solution of metal xanthogenate the following equilibrium holds:

$$\mathrm{MeX_2 \rightleftarrows Me^{2+} + 2X^-},$$

from which

$$L_{s\,\mathrm{MeX_2}} = [\mathrm{Me^{2+}}][\mathrm{X^-}]^2. \qquad (2)$$

On adding ammonia, the latter will complex metal ions $\mathrm{Me^{2+}}$ into a complex whose dissociation constant will be given by:

$$K_{\mathrm{Me(NH_3)_4^{2+}}} = \frac{[\mathrm{Me^{2+}}][\mathrm{NH_3}]^4}{[\mathrm{Me(NH_3)_4^{2+}}]}. \qquad (3)$$

From equation (1), we have:

$$K_e = \frac{[\mathrm{Me(NH_3)_4^{2+}}][\mathrm{X^-}]^2}{[\mathrm{NH_3}]^4}. \qquad (4)$$

According to formula (2): $[\mathrm{X^-}]^2 = \frac{L_{\mathrm{MeX_2}}}{[\mathrm{Me^{2+}}]}$, substituting this value in equation (4), we get:

$$K_e = \frac{[\mathrm{Me(NH_3)_4^{2+}}]L_{s\,\mathrm{MeX_2}}}{[\mathrm{NH_3}]^4[\mathrm{Me^{2+}}]},$$

or, taking into account formula (3),

$$K_e = \frac{L_{s\,\mathrm{MeX_2}}}{K_{\mathrm{Me(NH_3)_4^{2+}}}}. \qquad (5)$$

Comparing formulas (4) and (5), we have

$$\frac{[\mathrm{Me(NH_3)_4^{2+}}][\mathrm{X^-}]^2}{[\mathrm{NH_3}]^4} = \frac{L_{s\,\mathrm{MeX_2}}}{K_{\mathrm{Me(NH_3)_4^{2+}}}}. \qquad (6)$$

According to equation (1) $[\mathrm{X^-}] = 2[\mathrm{Me(NH_3)_4^{2+}}]$, substituting this value in equation (6), we have:

$$\frac{[\mathrm{X^-}]^2[\mathrm{Me(NH_3)_4^{2+}}]}{[\mathrm{NH_3}]^4} = \frac{2^2[\mathrm{Me(NH_3)_4^{2+}}]^2[\mathrm{Me(NH_3)_4^{2+}}]}{[\mathrm{NH_3}]^4} = \frac{4[\mathrm{Me(NH_3)_4^{2+}}]^3}{[\mathrm{NH_3}]^4} = \frac{L_{s\,\mathrm{MeX_2}}}{K_{\mathrm{Me(NH_3)_4^{2+}}}},$$

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*. Here and henceforth X denotes the xanthogenate anion.

from which

$$L_{s\,MeX_2} = \frac{4\,[Me(NH_3)_4^{2+}]^3 \cdot K_{Me(NH_3)_4^{2+}}}{[NH_3]^4}. \tag{7}$$

The concentration of ammonia in solution will be equal to the difference between total concentration of ammonia added as the aqueous solution and that amount of ammonia which has reacted with the metal.

Substituting this value in equation (7), we get:

$$L_{s\,MeX_2} = \frac{4\,[Me(NH_3)_4^{2+}]^3 \cdot K_{Me(NH_3)_4^{2+}}}{([NH_3]_{tot} - 4\,[Me(NH_3)_4^{2+}])^4}. \tag{8}$$

This equation enables one to calculate the solubility product of cadmium and nickel xanthogenates on the basis of the experimental results obtained. The concentration of the ammonia solution added was established by titration.

The following instability constants for the ammoniacal complexes of cadmium and nickel were used for calculation [2]:

$$K_{Cd(NH_3)_4^{2+}} = 1 \cdot 10^{-7};\ K_{Ni(NH_3)_4^{2+}} = 5 \cdot 10^{-9}.$$

Using these values the following results were obtained for the solubility products:

$$L_{s\,Cd(CH_3OCS_2)_2} = (4.6 \pm 1.3) \cdot 10^{-14}; \qquad L_{s\,Ni(C_2H_5OCS_2)_2} = (1.37 \pm 0.05) \cdot 10^{-12};$$

$$L_{s\,Cd(C_2H_5OCS_2)_2} = (5.6 \pm 0.6) \cdot 10^{-16}; \qquad L_{s\,Ni(C_3H_7OCS_2)_2} = (1.92 \pm 0.30) \cdot 10^{-17};$$

$$L_{s\,Cd(C_4H_9OCS_2)_2} = (3.4 \pm 2.0) \cdot 10^{-17}; \qquad L_{s\,Ni(C_4H_9OCS_2)_2} = (4.51 \pm 0.62) \cdot 10^{-18}.$$

$$L_{s\,Ni(CH_3OCS_2)_2} = (1.15 \pm 0.05) \cdot 10^{-14};$$

On comparing the values obtained for the solubility products of heavy metal xanthogenates, it becomes evident that with increasing molecular weight of the xanthogenate radical, the solubility of the respective heavy metal xanthogenate decreases; the exception proved to be nickel methylxanthogenate, which was less soluble than the ethylxanthogenate of the same metal. It is possible that the methylxanthogenate like the sulfide exists in several modifications.

The results obtained confirm the essential effect of "weighting" during formation of sparingly soluble compounds ("solid phase" reactions according to Kuznetsov [4]);this has been demonstrated by many investigators (see e.g. [5, 6])and has been given a theoretical foundation by Yatsimirsky [7]. The values obtained for the solubility products confirm the solubility series of heavy metal xanthogenates [1].

Iron Xanthogenate

The following equilibrium system was studied in order to determine the solubility product of iron xanthogenate:

$$FeX_3 + 3C_2O_4^{2-} \rightleftarrows [Fe(C_2O_4)_3]^{3-} + 3X^-. \tag{9}$$

The technique was the same as that used in the previous examples except that aqueous solutions of sodium oxalate were saturated with iron xanthogenate.

The following equilibrium exists in a saturated solution of iron xanthogenate:

$$FeX_3 \rightleftarrows Fe^{3+} + 3X^-.$$

rom which

$$L_{3\,FeX_3} = [Fe^{3+}]\,[X^-]^3. \tag{10}$$

n addition of oxalate ions to the solution, the oxalate ions will combine with iron to form a complex, whose nstability constant, according to results published by Babko and Dubovenko [3], is equal to:

$$K_{Fe(C_2O_4)_3^{3-}} = \frac{[Fe^{3+}]\,[C_2O_4^{2-}]^3}{[Fe(C_2O_4)_3^{3-}]} = 5.3\cdot10^{-17}. \tag{11}$$

rom equation (9), we have:

$$K_e = \frac{[Fe(C_2O_4)_3^{3-}]\,[X^-]^3}{[C_2O_4^{2-}]^3}. \tag{12}$$

ccording to formula (10):

$$[X^-]^3 = \frac{L_{3\,FeX_3}}{[Fe^{3+}]}.$$

ubstituting this value in equation (12), we get:

$$K_e = \frac{L_{3\,FeX_3}\cdot[Fe(C_2O_4)_3^{3-}]}{[Fe^{3+}]\cdot[C_2O_4^{2-}]^3};$$

r, taking into account formula (11), we have:

$$K_e = \frac{L_{3\,FeX_3}}{K_{Fe(C_2O_4)_3^{3-}}}. \tag{13}$$

Comparing equations (12) and (13), we get:

$$\frac{[X^-]^3\,[Fe(C_2O_4)_3^{3-}]}{[C_2O_4^{2-}]^3} = \frac{L_{3\,FeX_3}}{K_{Fe(C_2O_4)_3^{3-}}}. \tag{14}$$

According to equation (9): $[X^-] = 3\,[Fe(C_2O_4)_3^{3-}]$. Substituting this value in equation (14), we have:

$$\frac{[X^-]^3\,[Fe(C_2O_4)_3^{3-}]}{[C_2O_4^{2-}]^3} = \frac{3^3\,[Fe(C_2O_4)_3^{3-}]^3\,[Fe(C_2O_4)_3^{3-}]}{[C_2O_4^{2-}]^3} = \frac{27\,[Fe(C_2O_4)_3^{3-}]^4}{[C_2O_4^{2-}]^3} = \frac{L_{3\,FeX_3}}{K_{Fe(C_2O_4)_3^{3-}}},$$

from which

$$L_{3\,FeX_3} = \frac{27\,[Fe(C_2O_4)_3^{-3}]^4\cdot K_{Fe(C_2O_4)_3^{3-}}}{[C_2O_4^{2-}]^3} \tag{15}$$

The concentration of oxalate ions in solution is equal to the difference between the total concentration of the oxalate added (as sodium oxalate) and the amount of oxalate used for complexing the iron. Three oxalate ions are required for complexing each iron atom, accordingly:

$$[C_2O_4^{2-}]_{excess} = [C_2O_4^{2-}]_{total} - 3\,[Fe(C_2O_4)_3^{3-}].$$

Substituting this equation in (15), we get:

$$L_{s\,FeX_3} = \frac{27\,[Fe\,(C_2O_4)_3^{3-}]^4 \cdot K_{Fe\,(C_2O_4)_3^{3-}}}{([C_2O_4^{2-}]_{tot} - 3\,[Fe\,(C_2O_4)_3^{3-}])^3}. \tag{16}$$

This equation was used for calculating the solubility product of iron xanthogenate on the basis of experimental results. The following value was obtained for the solubility product of iron ethylxanthogenate:

$$L_{s\,Fe\,(C_2H_5OCS_2)_3} = (4.04 \pm 0.74) \cdot 10^{-20}.$$

SUMMARY

Equilibrium processes between cadmium and nickel xanthogenates and aqueous ammonia solutions have been studied, as well as those between sodium oxalate and iron ethylxanthogenate. The solubility of zinc xanthogenates in water has been determined. On the basis of the results obtained, the solubility products of the xanthogenates of the metals indicated have been calculated.

$$L_{s\,Zn\,(CH_3OCS_2)_2} = (2.85 \pm 0.5) \cdot 10^{-8};$$
$$L_{s\,Zn\,(C_2H_5OCS_2)_2} = (1.31 \pm 0.2) \cdot 10^{-9};$$
$$L_{s\,Zn\,(C_4H_9OCS_2)_2} = (3.76 \pm 0.91) \cdot 10^{-7};$$
$$L_{s\,Ni\,(CH_3OCS_2)_2} = (11.5 \pm 0.05) \cdot 10^{-14};$$
$$L_{s\,Ni\,(C_2H_5OCS_2)_2} = (1.37 \pm 0.05) \cdot 10^{-12};$$
$$L_{s\,Ni\,(C_3H_7OCS_2)_2} = (1.92 \pm 0.30) \cdot 10^{-17};$$
$$L_{s\,Ni\,(C_4H_9OCS_2)_2} = (4.51 \pm 0.62) \cdot 10^{-19};$$
$$L_{s\,Cd\,(CH_3OCS_2)_2} = (4.6 \pm 1.3) \cdot 10^{-16};$$
$$L_{s\,Cd\,(C_2H_5OCS_2)_2} = (5.6 \pm 0.6) \cdot 10^{-18};$$
$$L_{s\,Cd\,(C_4H_9OCS_2)_2} = (3.4 \pm 2.0) \cdot 10^{-17};$$
$$L_{s\,Fe\,(C_2H_5OCS_2)_3} = (4.04 \pm 0.74 \cdot 10^{-20}.)$$

The results obtained show that the solubility of the metal xanthogenates decreases with increasing molecular weight of the xanthogenate radical; the exception to this is nickel methylxanthogenate.

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THE ULTRAMICRO METHOD OF CHEMICAL ANALYSIS. AMPEROMETRIC TITRATION

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In an article published previously [1], taking potentiometric titration as an example, we demonstrated the possibility of using an electrochemical method of determining the end point during titration in volumes of the order of 10^{-3} ml. At the same time it is well known that in simplicity, accuracy, rapidity, and sensitivity, many amperometric methods are significantly better than potentiometric methods. The advantages of using the amperometric method in microanalysis, have been considered several times in the literature [2 - 4]. Kirk and coworkers [5] in 1950 showed that it was possible to use a vibrating platinum electrode during titrations in volumes of the order of 10^{-2} ml for determining tens and units of micrograms without having to use microscopes and manipulators. Nevertheless, it is precisely developments along this direction in ultramicro analysis that are of particular interest, since, by working on the stage of a microscope it is possible to cut down the amounts of materials required to the greatest possible extent.

Below is given a description of apparatus and technique for amperometric ultramicro titration under the microscope.

APPARATUS

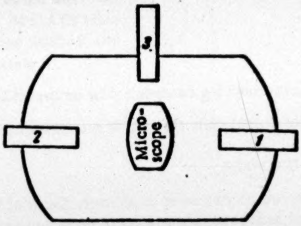

Fig. 1. Arrangement of manipulators during ultramicro-amperometric determinations:
1, 2, 3) manipulators.

For amperometric ultramicro titration, a microscope on whose stage is placed a humidity cabinet containing the tubes etc. used is required, as well as three manipulators in which are fitted a vibrating platinum electrode, a reference electrode, and a buret, respectively (Fig. 1).

In order that it should be possible to introduce all three instruments into the humidity cabinet [6] at the same time, it was left open on two sides and transverse grooves cut in one of the side walls; the bottom of the cabinet was lifted up so that it was higher than the screw of the stage. The platinum vibrating electrode, 0.2 mm in diameter and 2-3 mm long (Fig. 2) fitted in manipulator 3 was introduced through the transverse groove, while the reference electrode and buret whose tips had been turned through 90° were fitted in perpendicularly, the reference electrode and buret being fitted in manipulators 2 and 1 respectively.

Titration was carried out in the usual micro-vessel, which was placed in a holder in the humidity cabinet. The same holder which was a plexiglass plate with holes in it and covered with a stretched rubber ring (Fig. 3) was also used for containing the tubes with titrant, and solution to be titrated respectively.

The reference electrode was saturated calomel electrode; titrant was added by means of a buret fitted with a pressure micrometer described previously [1]. All tubes as well as the reference electrode were made hydrophobic before use [7]. The electrode was vibrated by an alarm, to the striking hammer of which was fused an insulated alarm conductor. The ring on its other end was fitted onto the capillary of the vibrating electrode.*

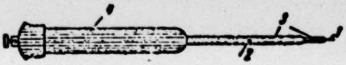

Fig. 2. Platinum electrode.
1) Platinum wire; 2) fine flex in plastic insulation; 3) glass capillaries; 4) ebonite holder

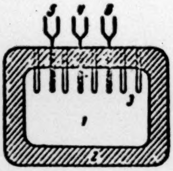

Fig. 3. Holder for vessels (tubes).
1) Plexiglass disc; 2) rubber ring; 3) holes in the disc; 4) titration tube; 5) and 6) tubes for solution to be titrated, and titrant respectively.

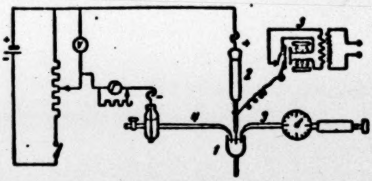

Fig. 4. General appearance of the cell and electric circuit for ultramicro amperometric titration.
1) titration vessel; 2) platinum vibrating electrode; 3) buret; 4) reference electrode; 5) vibrator setup.

Current was measured with a shunted galvanometer with a scale division of 1.4×10^{-9} amp.

The general appearance of the cell and electric circuit are shown on Fig. 4.

PROCEDURE

The vessel in which titration is to be carried out is brought into the field of vision of the microscope, and a definite volume of solution to be titrated introduced into it from the corresponding tube (see above) by means of a pipet held in manipulator 1. The buret is then fitted into manipulator 1 instead of the pipet.

The titration vessel is removed from the field of vision and the platinum electrode fitted into its center; to the left of the tip of the platinum electrode and at the same level is fitted the tip of the reference electrode, while to the right of the platinum electrode, and again at the same level as its tip, the tip of the buret is arranged; the tip of the buret is right in the focus of the field of vision.

The titration vessel is fitted round the electrodes and buret arranged as described, so that:

1) the platinum electrode runs through almost all the solution and is arranged freely in it without touching the vessel walls or the calomel electrode and buret tip;

2) the tip of the calomel electrode is not too deeply immersed in the solution;

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* The proportionality between concentration of test ion and current strength when the vibrating electrode is used in microanalysis has been demonstrated before. The value of the diffusion current can be increased by increasing the frequency of the current supplied to the vibrator [8].

3) the buret tip lies on the wall of the vessel.

Having connected the electric circuit (but not including the accumulator) and arranged the apparatus as described, the vibrator is switched on and the position of the platinum electrode adjusted so that it vibrates freely and efficiently in the solution. The accumulator is then connected up and the requisite voltage for the titration adjusted by means of a rheostat.

Titrant is added from the appropriate tube by means of a buret (see above); the galvanometer reading is noted together with the corresponding volume of titrant which is measured by reference to the readings on the micrometer; the position of the apparatus under the microscope is checked from time to time, and the tip of the calomel electrode adjusted as the volume of liquid increases. After the first appreciable shift in the galvanometer needle, another 4-5 readings are taken and a curve drawn.

Amperometric Ultramicro Determinations

Using the apparatus described, amperometric determinations were carried out using the oxidation-reduction method for the system V(V) — Fe(II) using the diffusion current of Fe^{2+} at 1.0 volt, and that of Fe^{3+} at +0.4 volt.

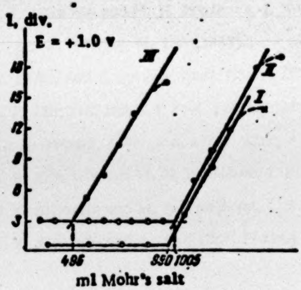

Fig. 5. Amperometric titration of ammonium vanadate with Mohr's salt at E = + + 1.0 volt.
I) 1 × 10^{-3} ml of 0.01 N solution; II) 1 × × 10^{-3} ml of 0.001 N solution; III) 0.5 × × 10^{-3} ml of 0.001 N solution.

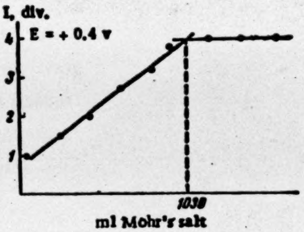

Fig. 6. Amperometric titration of 1 × × 10^{-3} ml of 0.001 N ammonium vanadate with Mohr's salt at E = + 0.4 volt.

The results obtained are given in the Table and are represented graphically by the curves on Figs. 5 and 6. On using more dilute solutions (which, in principle, is possible for amperometric titration) correspondingly smaller amounts of material can be determined.

Titration of Ammonium Vanadate with Mohr's Salt

Voltage in volts	Titrant (Mohr's salt)		Solution of vanadate titrated		Amount, in g		Error, in %
	concentration, N	Used, in ml	concentration, N	Volume, in ml	taken	found	
+1.0	0.01	$0.99 \cdot 10^{-3}$	0.01	$1 \cdot 10^{-3}$	$5.10 \cdot 10^{-7}$	$5.06 \cdot 10^{-7}$	—0.9
	0.001	$4.96 \cdot 10^{-4}$	0.001	$5 \cdot 10^{-4}$	$2.55 \cdot 10^{-8}$	$2.53 \cdot 10^{-8}$	—0.8
	0.001	$1.005 \cdot 10^{-3}$	0.001	$1 \cdot 10^{-3}$	$5.10 \cdot 10^{-8}$	$5.12 \cdot 10^{-8}$	+0.5
+0.4	0.001	$1.03 \cdot 10^{-3}$	0.001	$1 \cdot 10^{-3}$	$5.20 \cdot 10^{-8}$	$5.24 \cdot 10^{-8}$	+1.0

The authors wish to express their thanks to Van Yun-Yui of the Chinese Academy of Sciences for his experimental results which he communicated to us; these results were obtained when this technique was tried out in the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR.

SUMMARY

1) An apparatus has been devised and a technique developed for carrying out amperometric ultramicro titration on the object stage of a microscope, using volumes of $10^{-3} - 10^{-4}$ ml.

2) Results which have been obtained by means of this apparatus and technique have demonstrated the high experimental accuracy of this method and its good reproducibility.

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POLAROGRAPHIC DETERMINATION OF STRONTIUM

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Strontium has only been determined polarographically either in dilute aqueous solution (with a concentration of 0.001 M and less) [1-3], or in alcoholic and aqueous-alcoholic solutions [4]. Under these conditions the maxima on current – voltage curves are insignificant and there is no need to use surface active materials.

Nevertheless it sometimes occurs in chemical practice and also during determination of the solubility in water of certain sparingly soluble strontium salts, that the necessity arises of dealing with aqueous solutions with concentration greater than 0.001 M. Addition of alcohol in such cases is undesirable, since the alcohol depresses the height of the polarographic wave of strontium.

In the present article conditions are described for polarographic determination of strontium in solutions of its salts in which the concentration is greater than 0.001 M, and in which alcohol is not used.

The work was carried out on a recording polarogram model Odessa 6[*] whose galvanometer had a vibration period of 5.8 seconds, $R_{\text{internal resistance}} = 2.56\ \Omega$ and $R_{\text{crit.}} = 644\ \Omega$.

The accumulator used had a potential of 3.5 volt. Solutions were polarographed in a thermostat at 25 ± 0.2°. The dropping rate of the mercury was 1.9 seconds at a voltage of 0 volt. Most of the experiments were carried out with strontium chloride. The half-wave potential of strontium is –2.10 volt.

Results of the first experiments showed that maxima appear on the polarographic curves at concentration of $SrCl_2$ of 0.001 M when lithium chloride or tetraethyl-ammonium iodide were used as supporting electrolyte. These maxima increased with increasing strontium concentration. When the maxima were present no direct proportionality was observed between the value of the limiting current and strontium concentration in solution. When tetraethylammonium iodide was used as supporting electrolyte, the limiting current was lower than when lithium chloride was used as the supporting electrolyte (Table 1).

TABLE 1

Relation Between Limiting Current and Supporting Electrolyte Used

$SrCl_2$ in moles/liter	I_d, μ amp., at S = 1/50	
	LiCl, 0.1 N solution	$[N(C_2H_5)_4]I$, 0.1 N solution
0.0005	2.99	2.99
0.001	7.80	5.85
0.005	48.10	26.00
0.01	109.20	41.60

Thus strontium also demonstrates the existence of that phenomenon known in polarography of a change in the value of the limiting current on altering the supporting electrolyte [5]. In order to try and suppress the maxima on the polarographic curves of strontium we studied the effect of additions of some surface active agents (gelatine, Methyl Red, Phenolphthalein, and agar-agar); they were added dropwise as 1% solutions. It was found that Phenolphthalein and Methyl Red, even when added in appreciable amounts (up to 30 drops) had no effect on the maxima at all. Only gelatine proved effective.

On Figs. 1 and 2 are shown polarographic waves for strontium, obtained on adding various amounts of gelatine to

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[*] Some curves were checked on an other type of instrument, the SGM-8 model made by "Geologorazvedka" in 1954.

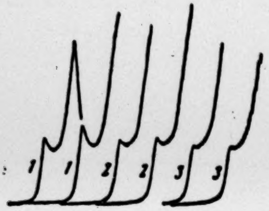

Fig. 1. Suppression of maxima on polarographic curves of strontium – 20 ml 0.005 M $SrCl_2$ in 0.1 N$[N(C_2H_5)_4]I$; S = 1/500. Additions of gelatine: 1) 5 drops; 2) 8 drops; 3) 10 drops.

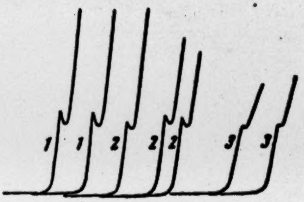

Fig. 2. Suppression of maxima on polarographic curves of strontium – 20 ml of 0.005 M $SrCl_2$ in 0.1 N LiCl; S = 1/500 Additions of gelatine: 1) none; 2) 2 drops; 3) 5 drops.

solutions of $SrCl_2$ in lithium chloride and tetraethylammonium iodide solutions as supporting electrolytes respectively.

It was found that with increasing strontium concentration in solution, the amount of gelatine which had to be added to suppress maxima increased. When maxima had been suppressed, it was found in both cases that waves were obtained whose heights could be used for the fairly accurate quantitative determination of strontium in solution. Under such conditions, in all cases there was observed a proportionality between the value of the limiting current and the concentration of strontium in solution; the constancy (within the limits to which readings can be taken) of the value of K in the equation $I_d = K{\cdot}c$ (Table 2) testifies to this.

TABLE 2

Relation Between Value of Limiting Current and Strontium Concentration in Solution

$$S = \frac{1}{500}\ (0.1\ N\ LiCl)$$

$c \cdot 10^3$ *	I_d, μ amp	I_d, μa mean	$K = \frac{I_d}{c \cdot 10^3}$
0.00892	32.5; 32.5	32.5	3.63
0.01325	49.4; 49.5; 49,4	48.1	3.63
0.01785	63.7; 65.0	64.4	3.61
0.02677	95.7 96.2	96.9	3.62

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* c-) the amount in g of Sr^{2+} (as $SrCl_2$) in 20 ml of solution

The effect of the anion of the strontium salt on the polarographic waves of strontium was also studied. Curves obtained for equimolar solutions of the following salts: $SrSO_4$, $SrCl_2$, $Sr(NO_3)_2$, $SrSeO_4$, $Sr(C_2H_3O_2)_2$ in a supporting electrolyte of LiCl, and of $[N(C_2H_5)_4]I$, showed that the wave heights were the same in all cases, with the exception of $Sr(NO_3)_2$, where the wave height was double. In the case of this salt wave height depends on the concentration of both the ions which form it, since the reduction potentials of NO_3^- and strontium from 0.1 N LiCl and $[N(C_2H_5)_4]I$, coincide [6]. Thus, for quantitative polarographic determination of strontium in various compounds, standard solutions may be prepared from strontium chloride or acetate.

SUMMARY

Conditions are described for polarographic determination of strontium in aqueous solutions of its salts at concentrations greater than 0.001 M.

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THE USE OF ASCORBIC ACID IN AMPEROMETRIC TITRATION

PART 1. DETERMINATION OF VANADIUM AND CERIUM IN THE PRESENCE OF OTHER ELEMENTS

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Ascorbic acid belongs to the class of mild reducing agents. Ptitsyn and Kozlov [1] have shown that ascorbic acid can be successfully used for determining Fe^{3+}. Nevertheless, the instability of ascorbic acid solutions which is connected with its ease of oxidation to dehydroascorbic acid, has, for a long time, prevented the wider use of this reagent in analytical practice. Erdey and Bador [2] have established that addition of Complexone III and formic acid increases the stability of ascorbic acid solutions considerably, prevents their oxidation by atmospheric oxygen, and enables titration to be carried out in open vessels. It is this fact which establishes the superiority of ascorbic acid over other reducing agents (Mohr's salt, salts of trivalent titanium, and divalent chromium salts). According to Borsook's results [3], the normal oxidation-reduction potential of ascorbic acid is equal to +0.40 volt; it is strongly dependant on the pH of the medium. Erdey and Bador [4 - 7] have developed an ascorbimetric determination of Fe^{3+}, ClO_3^-, IO_3^-, BrO_3^-, VO_3^- and Ce^{4+}. According to Skobets [8], ascorbic acid is oxidized on a rotating platinum electrode; this fact can be made use of for amperometric titration with this reagent of many oxidizing agents which do not give an electrode reaction during anodic polarization of a platinum electrode.

TABLE 1

Relation between $E_{1/2}$ and pH of the Supporting Electrolyte for a Constant Ascorbic Acid Concentration (4.5×10^{-4} N)

Supporting electrolyte	$E_{1/2}$ in v.
pH 6.81(phosphate buffer)	+0.38
pH 4.60 (acetate buffer)	+0.68
0.1 N H_2SO_4	+0.92
1 N H_2SO_4	+1.00

Ascorbic acid has been used as a reducing agent for the amperometric determination of iron in clays, refractory clays, and bauxites, determination being based on the reduction current of Fe^{3+} [9]. The aim of the work described here was to study the conditions for amperometric titration of certain oxidizing agents (VO_3^-, Ce^{4+}, $Fe(CN)_6^{3-}$, ClO_3^-, IO_3^-, etc) by means of ascorbic acid.

Ascorbic acid gives a clearly defined oxidation wave on the rotating platinum electrode (Fig. 1). For amperometric titration, it is important to establish the potential range and ascorbic acid concentrations at which the diffusion current for the oxidation of ascorbic acid is directly proportional to its concentration. Current – voltage curves were taken for solutions with various concentrations of ascorbic acid in 0.1 N H_2SO_4 as supporting electrolyte. With decreasing ascorbic acid concentrations it was found that the value of $E_{1/2}$ shifted to more positive potentials (Fig. 2), while it increased with increasing acidity of the solution (Table 1).

The equation $I_d = KC$ only holds up to a certain ascorbic acid concentration (10^{-3} M) (Fig. 3). During establishment of the equivalence point on the basis of the appearance of a current as a result of oxidation of ascorbic acid, titration must be carried out at potentials of +0.8 to 1.0 volt with respect to the saturated calomel electrode.

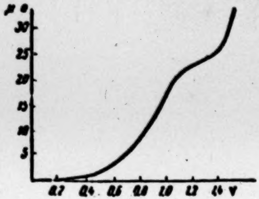

Fig. 1. Current-voltage curve for oxidation of ascorbic acid 4.5 x 10^{-4} N in a supporting electrolyte of 0.1 N H_2SO_4.

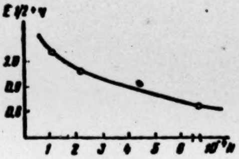

Fig. 2. Relation between $E_{1/2}$ and ascorbic acid concentration.

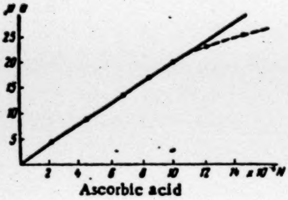

Fig. 3. Relation between I_d and ascorbic acid concentration.

Acorbic acid solutions were prepared by dissolving ascorbic acid sold for medicinal purposes. A 0.05 N solution was prepared by dissolving 4.4 g of the solid in distilled water in a 1 liter standard flask, and adding 4 ml of 75% formic acid and 0.1 g of Complexone III.

The solution was standardized potentiometrically agains KIO_3 [10].

Amperometric Determination of Quinquevalent Vanadium

In a supporting electrolyte of 0.1 N H_2SO_4, quadrivalent vanadium does not give a wave in the anodic region, while quinquevalent vanadium, starting at a potential of +0.2 volt, gives a weak reduction current (Fig. 4).

A 0.03925 M solution of ammonium vanadate was prepared by taking the exact amount of recrystallized solid analytical grade material. Titration was carried out with a solution of 0.05 M ascorbic acid at +0.9 volt. Titration curves are shown on Fig. 5.

Accurate and reproducible results were obtained at acid concentrations not exceeding 1 N H_2SO_4 (Table 2).

By using a 0.005 N solution of reagent in a supporting electrolyte of 0.1 N H_2SO_4, it was possible to determine with sufficient accuracy (on an average 2-3%) such amounts of vanadium as would require not less than 0.1 ml of ascorbic acid solution. Thus, in a supporting electrolyte of 0.1 N H_2SO_4 it was found possible to determine up to 0.04 mg of V with an error of ±0.001 mg in 10 ml of solution.

Nickel, manganese, zinc, aluminum, and chromium – the normal components of high alloy steel – do not interfere with titration of quinquevalent vanadium with ascorbic acid, since the ions of these elements do not give an electrode reaction on a platinum electrode in the anodic region. In the presence of the ions listed, in amounts which are one hundred times that of vanadium, results obtained for vanadium determinations with ascorbic acid are fully satisfactory (Table 3).

Sexivalent molybdenum does not react with ascorbic acid ($E_{0\,Mo^{VI}/Mo^{V}} = +\ 0.50$ volt) and in small amounts does not interfere with amperometric determination of vanadium. At a ratio of Mo:V > 20:1 high results are obtained, while at ratios of 40:1 vanadium could not be determined at all. It is possible that it may be in the form of vanadomolybdic acid. Actually it was observed that the solution became appreciably blue in color, the intensity of the color increasing with time as a result of reduction of molybdenum to vanadomolybdic acid. Good results were only obtained for determination of vanadium with ascorbic acid in the presence of tungsten for a

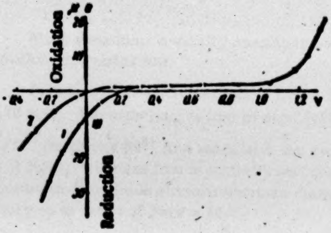

Fig. 4. Current-voltage curves:
1) Quinquevalent vanadium; 2) quadrivalent vanadium in a supporting electrolyte of 0.1 N H_2SO_4.

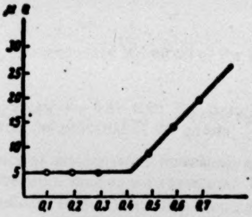

Fig. 5. Curve for amperometric titration of quinquevalent vanadium with ascorbic acid.

ratio of W:V = 1:1. (Table 5). When large amounts of tungsten were present, the results obtained were low, presumably as a result of formation of vanadotungstic acid. Quadrivalent titanium ($E^{\circ}_{Ti^{IV}/Ti^{III}} = -0.046$ volt) does not interfere with amperometric titration of vanadium with ascorbic acid (Table 4). Amperometric determination of vanadium is to be preferred to the photometric method using hydrogen peroxide, since titanium interferes with the latter method.

TABLE 2

Amperometric Determination of Vanadium at Various Acidities of the Supporting Electrolyte

Supporting electrolyte	Vanadium, mg		Error, in mg	Supporting electrolyte	Vanadium, mg		Error, in mg
	taken	found			taken	found	
0.1 *N* H_2SO_4	0.40	0.38	−0.02		0.100	0.097	−0.003
	0.80	0.79	−0.01		0.060	0.059	−0.001
	1.20	1.18	−0.02		0.040	0.040	+0.00
	1.60	1.60	0	1 *N* H_2SO_4	1.00	1.01	+0.01
	0.200	0.199	−0.001		2.00	2.02	+0.02
	0.200	0.200	±0	2 *N* H_2SO_4	1.00	1.27	+0.27
	0.160	0.165	+0.005	10 *N* H_2SO_4	1.00	1.37	+0.37

TABLE 3

Determination of Quinquevalent Vanadium in the Presence of Nickel, Manganese, Zinc, Aluminum, and Chromium

Amount added, mg					Vanadium, mg		Error, in mg
Ni	Mn	Zn	Al	Cr	taken	found	
60	—	—	—	—	2.00	2.02	+0.02
300	—	—	—	—	1.00	1.01	+0.01
600	—	—	—	—	2.00	2.01	+0.01
—	120	—	—	—	1.0	0.99	−0.01
—	160	—	—	—	1.00	1.01	+0.01
—	—	50	—	—	1.00	0.97	−0.03
—	—	100	—	—	1.00	1.009	+0.009
—	—	—	50	—	1.00	0.99	−0.01
—	—	—	100	—	1.20	1.21	+0.01
—	—	—	—	300	1.00	19.01	+0.01
				60	1.20	1.20	0

Since vanadium is usually accompanied by iron, it was very important to study the effect of the latter on vanadium determination.

Quinquevalent vanadium should titrate before trivalent iron ($E_{0}{}_{V^V/V^{IV}}$ = + 0.89 volt; $E_{0}{}_{Fe^{III}/Fe^{II}}$ = + +0.76 volt). Nevertheless, as ions of quadrivalent vanadium accumulate, the potential of the system V^V/V^{IV} drops and Fe^{3+} ions react with the ascorbic acid; in the presence of quinquevalent vanadium, even in 0.1 N H_2SO_4, trivalent iron is partially reduced with ascorbic acid at the same time as the vanadium. This is demonstrated by the low results obtained during determination of vanadium (Table 5); titration results are satisfactory up to ratios of Fe:V = 10:1.

TABLE 4

Determination of Quinquevalent Vanadium in the Presence of Sexivalent Molybdenum and Tungsten, and Quadrivalent Titanium

Added, mg			Vanadium, mg		Error, mg
Mo	W	Ti	taken	found	
1	—	—	1.00	0.99	—0.01
10	—	—	1 00	1.00	+0
20	—	—	1.00	1.02	±0.02
30	—	—	1.00	0.75	—0.25
—	1	—	1.00	0.99	—0.01
—	2	—	1.00	0.90	—0.10
—	—	25	1.00	1.01	+0.01
—	—	50	1.00	0.97	—0.03

TABLE 5

Determination of Vanadium in the Presence of Iron

Iron	Vanadium, mg		Error, mg
taken	taken	found	
—	1.00	1.01	+0.01
—	5.00	5.02	+0.02
4	1.00	0.98	—0.02
6	1.00	0.98	—0.02
10	1.00	0.95	—0.05
20	1.00	0.90	—0.10
20	5.00	5.02	—0.02
60	5.00	4.99	—0.01
100	5.00	4.91	0.09

For determination of vanadium in the presence of large amounts of iron, the latter was removed chromatographically [10]. Test solution acidified with sulfuric acid and containing H_2O_2 in an amount five times that of vanadium was passed through column of cation exchange resin SBS in the H form; the column was then eluted with 1% H_2O_2 in 0.1 N H_2SO_4.

Hydrogen peroxide in the eluate was destroyed with a 5% solution of potassium permanganate; the latter was added dropwise until a rose color appeared which did not disappear for 10 minutes. Excess permanganate was removed by dropwise addition of a saturated solution of oxalic acid. The solution with a volume of 70-80 ml was transferred to a 100 ml flask and made up to the mark; 25 ml was taken for titration. Using this technique, good results were obtained for vanadium at ratios of Fe:V of 50:1 and 100:1.

This amperometric method of determining vanadium with ascorbic acid was used for steel analysis. A sample of steel containing vanadium was dissolved by the usual method [12]. To 25 ml of the solution thus obtained was added 25% NH_4OH until the ferric hydroxide which started to separate out from solution did not redissolve on shaking the solution. The small amount of precipitate which separated out was dissolved in a few drops of 1 N H_2SO_4: iron and vanadium were then separated from each other by the chromatographic technique described. Results of determination of vanadium in steels are given in Table 6.

Amperometric Determination of Cerium

The normal oxidation-reduction potential of the system Ce^{IV}/Ce^{III} E_0 = 1.55 depends to only a very small extent on acidity, and, consequently, for quantitative determination of cerium, ascorbic acid can be used as a reducing agent as well as other reducing agents. The solution of cerium sulfate was prepared from analytical grade salt. The solution was standardized potentiometrically against Mohr's salt.

Titration was carried out on the basis of the reduction current of Ce^{4+} at a potential of −0.1 to +0.5 volt, when ascorbic acid does not yet give an oxidation current. The acidity of the solution has an important effect on titration results. Optimum results were obtained at an acidity of not less than 2 N H_2SO_4 (Table 7). 0.35 mg of Ce can be determined in 10 ml of solution. A vibrating platinum micro-electrode (Table 8) was used for determining cerium in small volumes (2 ml).

TABLE 6

Determination of Vanadium in Steels*

Steel anal. stand. sample	Specified vanadium content, %	Vanadium found, %		Error, in %	
122-a	1.85	1.78	1.89	−0.07	+0.04
156	1.50	1.47	1.55	−0.03	+0.05

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* The steel was reported to have the following composition:

Steel 122a Chromium-tungsten-vanadium (in %)

C	Mn	Si	P	S	Cr	Ni	W	V
0.88	0.25	0.14	0.019	0.030	0,17	0.20	8.80	1.85

Steel 156-Instrumental-Fast Cutting Cobalt Steel (in %)

C	Mn	P	S	Si	Co	Mo	Cr	Ni	W	V
0.79	0.34	0.028	0.014	0.30	10.50	0.51	4.66	0.28	17.06	1.50

By changing the acidity of the medium, it is possible to increase the specificity of the reducing action of ascorbic acid. By increasing the acidity, which leads to an increase in the oxidation-reduction potential of ascorbic acid, we succeeded in preventing reduction of trivalent iron. Ascorbic acid only reduces trivalent iron in weaklyacid media (pH about 1.5); increasing the acidity leads to a decrease in reaction rate so that in 2 N H_2SO_4 hardly any iron is reduced even on heating. Best results for amperometric titration of cerium with ascorbic acid, for stoichiometric reaction of the components, were obtained at an acidity of 5 N with respect to H_2SO_4. Under these conditions trivalent iron does not react with ascorbic acid, and consequently, does not interfere with cerium determination. Cerium was titrated at a potential of +0.3 to 0.5 volt.

TABLE 7

Titration of Cerium with Ascorbic Acid (Volume 10 ml)

Supporting electrolyte	Ce, in mg		Error, mg
	taken	found	
0.01 *N* H_2SO_3	0.811	0.610	0.201
2 *N* H_2SO_4	0.811	0.765	−0.046
»	0.811	0.791	−0.020
5 *N* H_2SO_4	0.406	0.402	−0.004
»	0.406	0.402	−0.002
10 *N* H_2SO_4	0.325	0.324	−0.001
	0.406	0.402	−0.004

TABLE 8

Determination of Cerium with a Vibrating Platinum Electrode in a Volume of 2 ml

Ce, in mg		Error, in mg
taken	found	
0.568	0.570	+0.002
0.406	0.410	+0.004
0.406	0.406	0
0.203	0.206	+0.003
0.203	0.204	+0.001

When reaction with cerium was complete, as established by a drop in cathode current to zero, concentrated ammonia was added to the titration vessel dropwise until a turbidity of ferric hydroxide appeared; this precipitate was then dissolved by dropwise addition of 0.1 N H_2SO_4; the solution was heated to 50-60° and titration potential altered ("0" instead of +0.3 - +0.5 volt); titration was then continued until the diffusion current for reduction of trivalent iron dropped to zero. The equivalence point was determined graphically.

Results for determination of cerium and iron in the same solution by means of ascorbic acid are given in Table 9.

TABLE 9

Determination of Cerium and Iron Present together in Solution

Ce, in mg		Error, in mg	Fe, in mg		Error, in mg
taken	found		taken	found	
1.62	1.56	−0.06	1.98	1.95	−0.03
1.62	1.62	±0	1.98	1.90	−0.08
1.62	1.60	−0.02	1.98	1.98	±0
1.62	1.63	+0.01	3.96	3.92	−0.04
0.81	0.80	−0.01	9.90	9.95	+0.05
0.81	0.78	−0.03	9.90	9.84	−0.06

The method which we have suggested for the successive determination of cerium and iron, together with the method suggested earlier for determination of iron and vanadium [13], molybdenum and a number of other elements [14], demonstrate the great possibilities of the amperometric titration method.

SUMMARY

1) Ascorbic acid is oxidized on a rotating platinum micro-electrode; the half-wave potential depends on the acidity of the solution and on reagent concentration. The equation $I_d = Kc$ is observed up to solutions with a concentration of 10^{-5}N.

2) A solution of ascorbic acid stabilized with Complexome III and formic acid can be used successfully as a reagent for amperometric titration using oxidation-reduction reactions.

3) Ascorbic acid can be used for determining vanadium in pure salts, and in the presence of nickel, manganese, zinc, aluminum, chromium, and titanium and also in the presence of iron, molybdenum, and tungsten.

4) A method has been developed for determination of cerium in pure salts, and conditions have been established for amperometric determination of quadrivalent cerium and trivalent iron with ascorbic acid.

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* [See C.B. translation.]

INVESTIGATION OF SOME AZO DYES AS REAGENTS FOR INDIUM

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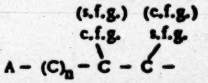
During a study of some colored reagents, Kulberg [1] showed that the functional analytical group for indium can be represented as follows*:



$$A-(C)_n-\overset{\overset{\text{(s.f.g.)}}{\text{c.f.g.}}}{\overset{\backslash}{C}}-\overset{\overset{\text{(c.f.g.)}}{\text{s.f.g.}}}{\overset{/}{C}}-$$

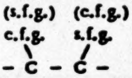
where

c.f.g. is – OH – SH = O.

s.f.g. is — OH – SH – COOH.

This group is present in the molecules of alizarin, alizarin S, quinalizarin, aluminon, and other reagents.

We investigated the possibility of using a series of azo dyes containing the group



$$-\overset{\overset{\text{(s.f.g.)}}{\text{c.f.g.}}}{\overset{\backslash}{C}}-\overset{\overset{\text{(c.f.g.)}}{\text{s.f.g.}}}{\overset{/}{C}}-$$

analogous to that described by L. M. Kulberg, as reagents for indium ions in various media. It was found that some azo dyes (Table 1) which contain this group give a color reaction for indium in the presence of 2 N acetic acid.

The OH group must be regarded as the salt forming group, while the complex forming group is the nitrogen of the azo group.

The possibility of forming inner complex rings in which the metal ion is connected by a subsidiary valency with the azo group nitrogen has been pointed out by Kuznetsov [2] and Kulberg [3] in the case of zirconium and thorium.

Our subsequent studies showed that the presence of one of the groups mentioned in a dye is not sufficient on its own for making use of this dye as a reagent for indium ions. Thus, some azo dyes, while they contain this group, still did not give a positive reaction with indium (Table 2).

From a comparison of structural formulas it follows that all azo dyes which do react with indium salts (Table 1) have, in addition to the group indicated, a nitro group as well in the para position with respect to the hydroxyl group or in the meta position with respecto to the azo group. Azo dyes which contain the nitro group in the ortho position to the azo group, do not give color reactions with indium ions (Table 2). Presumably, the presence of a nitro group in the para position increases the capacity to react with indium. The medium, as Kuznetsov has shown [4], has an essential effect on reaction sensitivity. We determined the sensitivity and specificity of the reactions with azo dyes 1-7 at various pH values of the medium. At the same time we studied the conditions for carrying out reactions for indium salts using gallein and gallocyanine, which Kulber [5] studied during establishment of functional-analytical groups for indium. For comparison, we also carried out reactions with the most widely used reagents for indium – alizarin and quinalizarin – under the same conditions as we used for the study of the azo dyes.

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* c.f.g. is the complex forming group; s.f.g. is the salt forming group.

TABLE 1

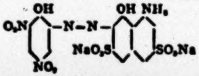
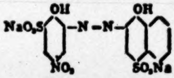
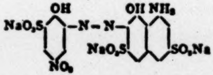
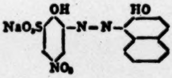
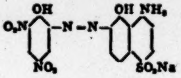
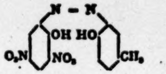
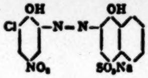
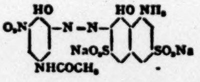
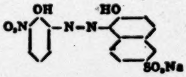
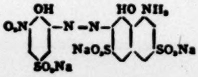
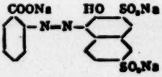
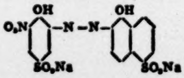
Reagent number	Formula	Reagent number	Formula
1		5	
2		6	
3		7	
4			

TABLE 2

Reagent number	Formula	Reagent number	Formula
8		11	
9		12	
10			

To 0.03 ml of a solution of an indium salt was added 0.06 ml of a buffer solution with the appropriate pH values, and 0.03 ml of a 0.05-0.1% solution of the azo dye, and development of color observed. Blank tests were carried out at the same time. The colors observed are noted in Table 3.

It is interesting to observe that dyes 1-3 which contain an amino group give a blue color, while dyes 4-7 which do not contain an amino group, give a rose color with indium salts. The sensitivity of the reaction for indium depends to a considerable extent on pH (Table 4).

TABLE 3

Reagent	pH of solution	Color of solution	
		In the absence of In	In the presence of In
Alizarin	5–6	Yellow	Red
Quinalizarin	5–6	Yellow	Rose-violet
1	5–7	Rose-violet	Blue
2	4–7	Rose-violet	Blue
3	4–5	Rose-violet	Blue*
4	5–6	Dirty grey	Rose
5	4–7	Cherry	Rose
6	5–6	Rose-violet	Rose
7	4–7	Yellow	Rose
Gallein	3–5	Dirty grey	Rose
Gallocyanine	3–6	Rose-violet	Violet

TABLE 4

Reagent	Limiting concentration at pH of solution equal to				
	3	4	5	6	7
Alizarin	—	—	1 : 10 000	1 : 10 000	—
Quinalizarin	—	—	1 : 15 000	1 : 15 000	—
1	—	—	1 : 15 000	1 : 1000	1 : 1000
2	—	1 : 1000	1 : 20 000	1 : 100	1 : 1000
3	—	1 : 1000	1 : 1000	—	—
4	—	—	1 : 1000	1 : 1000	—
5	—	1 : 5000	1 : 10 000	1 : 1000	1 : 1000
6	—	—	1 : 1000	1 : 1000	—
7	—	1 : 15 000	1 : 15 000	1 : 5000	1 : 1000
Gallein	1 : 1000	1 : 5000	1 : 5000	—	—
Gallocyanine	1 : 5000	1 : 20 000	1 : 20 000	1 : 10 000	—

At pH of 2 and lower and pH 10 and higher, none of the reagents studied gave a reaction with indium.

From Table 4 it follows that the optimum value of the pH is 5; azo dye No. 2 and gallocyanine proved to be the most sensitive.

The difference in sensitivity at pH 5 of reagents similar in structure (e.g. 1, 2, 3) apparently depends on differences in the location of substituents in the molecule. All our further tests were carried out with reagents 1, 2, 5 and 7 and also with gallocyanine and quinalizarin which exhibit optimum sensitivity at pH 5. The interaction of these reagents with the salts of other metals is shown in Table 5.

The ions of many heavy metals react with the dyes studied in addition to indium (Table 5). Nevertheless, in most cases the sensitivity of these reagents is small. The limiting concentrations are usually equal to 1:100-1:1000, sometimes 1:10,000. In individual cases for example, the sensitivity of the reaction for cobalt salts when reagent 1 is used amounts to 1:2,000,000, while for nickel salts with reagent 7 it amounts to 1:100,000.

Experiments also showed that reagents 1 and 2 enable indium to be detected in the presence of aluminum. The reagents for indium described previously also react with aluminum.

We studied the possibility of detecting indium in the presence of other metals (Table 6).

It follows from Table 6 that only reagent 2 makes it possible to detect indium in the presence of a comparatively large number of other salts. In order to reduce the effect of other cations we carried out reactions for indium in the presence of a 1% solution of sodium fluoride (Table 7).

TABLE 5

Reagent No. or name / Cations	1	2	5	7	Gallocyanine	Quinalizarin
	Color of the solution					
Control test	Rose-violet	Rose-violet	Cherry	Yellow	Rose-violet	Yellow
Ce^{3+}	Blue	—	Red	Rose	Violet	Violet
La^{3+}	Blue	—	Red	—	Violet	Violet
Nd^{3+}	Blue	—	—	Rose	—	Violet
Zr^{IV}	—	—	—	—	—	Violet
Th^{4+}	Blue	—	Red	Rose	Violet	Violet
UO_2^{2+}	Blue	Blue		—	Rose	Dirty grey
Al^{3+}	—	Red	Red	Rose	Violet	Red
Cr^{3+}		—	Orange	—	Red	
Fe^{3+}	Rose	Rose	Brown	—	Violet	—
Mn^{2+}	—	—		Rose	—	—
Ni^{2+}	Blue	—	—	—	—	—
Co^{2+}	Blue	—		—		
Zn^{2+}	Blue	Blue	Red	Rose	—	
Cu^{2+}	Blue	Blue	Red	Rose		Violet
Sb^{3+}	Red	Red		—	—	—
Pb^{2+}		—		—		
Sn^{2+}	Red	Red		—		Rose precipitate
Cd^{2+}	Red	Red		—		—

TABLE 6

Reagent / Cations	1	2	5	7	Gallocyanine	Quinalizarin
	Limiting ratios at pH 5					
$In^{3+} : Al^{3+}$	1 : 80	1 : 80	1 : 1	1 : 20	1 : 1	1 : 1
$In^{3+} : Fe^{3+}$	1 : 2	1 : 2	1 : 1	1 : 1	1 : 1	1 : 1
$In^{3+} : Th^{4+}$	1 : 2	1 : 15	1 : 1	1 : 1	1 : 1	1 : 1
$In^{3+} : UO^{2+}$	1 : 2	1 : 8	1 : 1	1 : 1	1 : 35	1 : 1
$In^{3+} : Ce^{3+}$	1 : 2	1 : 80	1 : 1	1 : 1	1 : 1	1 : 1
$In^{3+} : La^{3+}$	1 : 1	1 : 80	1 : 1	1 : 40	1 : 1	1 : 1
$In^{3+} : Zn^{2+}$	1 : 1	1 : 20	1 : 1	1 : 1	1 : 1	1 : 1
$In^{3+} : Mn^{2+}$	1 : 1	1 : 100	1 : 1	—	1 : 25	—
$In^{3+} : Mg^{2+}$	1 : 25	1 : 25	—	—	1 : 25	1 : 25

TABLE 7

Reagent / Cations	5	Gallocyanine	Quinalizarin
	Limiting ratios at pH 5		
$In^{3+} : Al^{3+}$	1 : 25	1 : 15	1 : 10
$In^{3+} : Th^{4+}$	1 : 25	1 : 25	1 : 5
$In^{3+} : Ce^{3+}$	1 : 25	1 : 75	1 : 15
$In^{3+} : La^{3+}$	1 : 10	1 : 25	1 : 5

On this basis therefore it can be concluded that reagents 2, 5, and gallocyanine give better results than quinalizarin and alizarin for detecting indium; these reagents can be used for detecting indium in solutions containing excess of other cations.

SUMMARY

1) A qualitative study has been made of the interaction of indium ions with a number of azo dyes, gallein, gallocyanine, quinalizarin, and alizarin.

2) The sensitivity of indium detection at various pH values has been established. Optimum sensitivity is observed at pH 5.

3) It has been shown that it is possible to detect indium in the presence of certain salts.

4) Some new reactions for indium are suggested.

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A TITRIMETRIC METHOD OF DETERMINING BISMUTH IN THE PRESENCE OF PHOSPHATES, SULFATES, OXALATES, SALICYLATES, AND HEAVY METALS

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Sparingly soluble compounds of bismuth readily dissolve even in 0.1 N solutions of mineral acids in the presence of chlorides, bromides, iodides, thiocyanates, oxalates, tartrates, and other salts which form readily soluble complexes with these bismuth compounds. An alkalimetric method of determining bismuth which has been worked out is based on the following: an aliquot of bismuth (0.02-0.05 g) is treated in a flask with 0.5-1.0 g of KI and 10-15 ml of 0.1 N H_2SO_4, and is heated until the salt has completely dissolved (when this is done, a polyiodide complex of bismuth $[BiI_X]^{3-X}$ is formed, which has an orange-red color); to the hot solution is added 10-15 ml of about 0.4 N $Na_2C_2O_4$ until the solution is colorless; after cooling the free acid is titrated with 0.1 N NaOH (B ml) using Methyl Red as indicator. A known excess of 0.1 N NaOH is next added to the mixture (in order to decompose the oxalate complex of bismuth), and the mixture boiled for 2-3 minutes, after which it is cooled and excess alkali titrated with 0.1 N H_2SO_4 using phenolphthalein as indicator (B_1 ml)

$$[BiI_x]^{3-x} + 3C_2O_4^{2-} \rightleftarrows [Bi(C_2O_4)_3]^{3-} + XI^-$$

$$[Bi(C_2O_4)_3]^{3-} + 3OH^- \rightarrow Bi(OH)_3 + 3C_2O_4^{2-}.$$

The difference between the total volume of 0.1 N alkali (A ml) and the volume of acid will correspond to the amount in mls of 0.1 N bismuth salt in the test solution (C ml)

$$A - (B + B_1) = C$$

This method was tried out first on solutions of bismuth nitrate which were standardized by evaporation of a known volume, calcination of the dry residue, and weighing it as bismuth oxide ($T_{Bi} = 0.00301$); it was subsequently tested out on synthetic mixtures containing the salts of various heavy metals, and mixtures containing the sulfates, oxalates, salicylates, and the phosphates of the alkali metals. In the latter case, 5 g of KCl is added to the solution before titration of free acid with alkali to the Methyl Red end point.

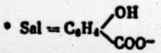
Results of some determinations are given in Table 1.

Determination of bismuth in the presence of heavy metals is of interest. Numerous articles have been devoted to this question. In particular, precipitation and determination of bismuth as the phosphate enables it to be separated from other heavy metals whose phosphates are readily soluble in mineral acids. Thus, Moser [1] has shown that bismuth phosphate is not soluble in 1.2 N nitric acid. Kovalenko [2, 3] found that bismuth phosphate does not dissolve in 0.4-09 N nitric acid. Zharovsky has made a detailed study of the solubility of bismuth phosphate in nitric acid [4]; he showed that on increasing nitric acid concentration tenfold, the solubility of bismuth phosphate increases about 20 times. Halides increase the solubility of bismuth phosphate in dilute nitric acid [5-8]. We found that bismuth phosphate dissolves even in 0.1 N solutions of mineral acids in the presence of small amounts of halides, particularly potassium iodide.

TABLE 1

(5 ml of $Bi(NO_3)_3$ solution containing 0.01505 g of Bi was taken)

Salt added, in g		NaOH used, ml	Bi found	
			In g	In %
		2.15	0.01503	99.84
0.2	Na_2SO_4	2.15	0.01503	99.84
0.1	Na_2HPO_4	2.15	0.01503	99.84
0.5	Na_2HPO_4	2.15	0.01503	99.84
0.1	SalNa*	2.16	0.01505	100.00**
0.2	SalNa	2.18	0.01518	100.76
0.1	$Na_2C_2O_4$	2.16	0.01505	100.00



* $Sal = C_6H_4\langle{}^{OH}_{COO^-}$

** The mixture was boiled for 10-15 minutes to remove salicylic acid.

Since bismuth phosphate is practically insoluble in dilute nitric acid and has a constant composition, it can be used for the removal and gravimetric quantitative determination of bismuth in salts, ores and various alloys [2, 9-15]. As tests showed the phosphate method can be used for determining bismuth in the presence of heavy metals and also a series of organic compounds such as: oxalates, salicylates, acetates, formates, urea etc. [16]. Gravimetric determination is possible only in the absence of such ions as sulfates, sulfides, and halides. Excess phosphate and other materials may contaminate the precipitate as a result of adsorption and coprecipitation.

The proposed alkalimetric method can be carried out in the presence of the ions listed.

EXPERIMENTAL PROCEDURE

To a boiling, weak nitric acid solution (about 0.5 N HNO_3) containing the bismuth salt and other heavy metals is added excess of approximately 0.1 N Na_2HPO_4. After boiling for two minutes the precipitate –$BiPO_4$– is filtered off and thoroughly washed with hot water. The washed precipitate is replaced in the vessel in which precipitation was carried out, and is dissolved in 10-15 ml of approximately 0.1 N H_2SO_4 in the presence of 0.5-1.0 g KI. The mixture is boiled for 2 minutes until the precipitate has dissolved completely and the polyiodide ion $[BiI_x]^{3-x}$ (where x = 4-7) has been formed. To the hot solution the requisite amount of approximately 0.4 N $Na_2C_2O_4$ is added from a buret to decolorize the solution; 5 g of KCl is then added; after cooling the solution (volume 20 ml) the procedure described above is followed.

Results of such determinations are given in Table 2.

TABLE 2

Test mixtures	Bi content of solution in g	0.1 N NaOH used, ml	Bi found	
			In g	In %
5 ml of a nitric acid solution of Bi^{3+} and 10 ml of 0.1 N $Pb(NO_3)_2$	0.01686	2.40	0.01672	99.17
5 ml of a nitric acid solution of Bi^{3+} + 25 ml of 0.1 N $Pb(NO_3)_2$	0.01686	2.43	0.01692	100 35
Ditto + 10 ml 0.1 N $ZnSO_4$	0.01686	2.40	0.01672	99.17
Ditto + 25 ml 0.1 N $ZnSO_4$	0.01686	2.43	0.01692	100.35
10 ml of bismuth nitrate + 5 ml of 0.1 N $AgNO_3$	0.03372	4.82	0.03358	99.58
Ditto + 10 ml 0.1 N $AgNO_3$	0.03372	4.83	0.03364	99.76
Ditto + 10 ml 0.1 N $Fe_2(SO_4)_3$	0.03372	4.83	0.03364	99,76
5 ml of bismuth nitrate + 25 ml of 0.1 N $Fe_2(SO_4)_3$	0.01686	2.42	0.01686	100.00
Ditto + 10 ml 0.1 N $Al(NO_3)_3$	0.01686	2.42	0.01686	100.00
Ditto + 25 ml 0.1 N $Al(NO_3)_3$	0.01686	2.42	0.01686	100.00
Ditto + 10 ml 0.1 N $CuSO_4$	0.01686	2.42	0.01686	100.00
Ditto + 10 ml 0.1 N $CdSO_4$	0.01686	2.42	0.01686	100.00
Ditto + 10 ml 0.1 N $Co(NO_3)_2$	0.01686	2.43	0.01692	100.35
Ditto + 10 ml 0.1 N $Co(NO_3)_2$	0.01686	2.42	0.01686	100.00

Some of the high values obtained are probably the result of coprecipitation. Determination of bismuth in the presence of large amounts of lead is of great practical interest.

Since lead sulfate is less soluble than lead iodide [17], it should be possible to use SO_4^{2-} for separating lead from bismuth with subsequent treatment of the sulfate precipitate with a solution of potassium iodide. Under these conditions only bismuth ions as the polyiodide complex go into solution, while the lead sulfate remains in the precipitate.

Such a method of analysis may be of practical interest under conditions where excess alkali metal sulfates do not increase the solubility of lead sulfate. The solubility of lead sulfate in water, nitric acid, and in solutions of various electrolytes with and without common ions has been studied by many authors [18-20]. Of special importance is the work of I. V. Tananaev and coworkers [21, 22]. They found that in the system $PbSO_4 - Me_2SO_4 - H_2O$, i. e. in the presence of a common ion, the solubility of $PbSO_4$ decreases with increasing Me_2SO_4 concentration; in 0.1 N solution of Me_2SO_4 they established the following solubility series for $PbSO_4$:

$$H_2O > LiSO_4 > Na_2SO_4 > K_2SO_4:$$

$$1.510^{-4};\ 1.15—10^{-5};$$
$$7.4—10^{-6};$$
$$3.55—10^{-6}\ \text{mole/liter}$$

The characteristic behavior of lead sulfate in potassium sulfate solutions is attributed by the authors to the fact that at low potassium sulfate concentrations (0.01-0.1 mole/liter) lead sulfate reacts with potassium sulfate to form the double salt $K_2SO_4 \cdot PbSO_4$. In relation to the latter salt, K_2SO_4 behaves as an electrolyte with two common ions (K^+, SO_4^{2-}) and the solubility of the lead sulfate will decrease even further. Accordingly, the most complete precipitation and separation of lead from bismuth ions can be achieved by adding potassium sulfate to the test mixture. Our experiments confirmed this conclusion.

TABLE 3

(2.42 ml of 0.1 N $Bi(NO_3)_3$, i.e. 0.01686 g of Bi was taken)

0.1 N $Pb(NO_3)_2$ aded, in ml	0.1 N NaOH used, in ml	Bi found	
		In g	In %
3.02	2.420	0.01686	100.00
3.02	2.420	0.01686	100.00
9.06	2.420	0.01686	100.00
9.06	2.400	0.01672	99.20
15.10	2.420	0.01686	100.00
15.10	2.420	0.01686	100.00
30.20	2.430	0.01692	100.35
30.20	2.420	0.01686	100.00

EXPERIMENTAL PROCEDURE

To weak nitric acid solutions of the lead and bismuth salts contained in 50 ml standard flasks is added excess 5-10 ml of a saturated solution of K_2SO_4 (11%). To the precipitates of $PbSO_4$ and $Bi_2(SO_4)_3$ which separate out is added 1 g of KI and the whole thoroughly shaken; after standing for 10 minutes the volume is made up to the mark with water, and the final mixture shaken and then filtered. To 25 ml of filtrate is added approximately 0.4 N $Na_2C_2O_4$ until a colorless solution is obtained; the free acid is titrated with 0.1 N NaOH using Methyl Red as indicator. The subsequent procedure is the same as described above.

Results of these determinations are given in Table 3.

SUMMARY

An alkalimetric method has been developed for the quantitative determination of bismuth in the presence of sulfates, oxalates, salicylates, phosphates, and heavy metals; this method is very convenient, is readily carried out, requires little time, and gives good results. The method can be recommended for quantitative determination of bismuth in the presence of heavy metals, and also in various other mixtures.

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POTENTIOMETRIC MICRO-TITRATION OF MANGANESE IN FERROUS AND NON-FERROUS METALS AND ALLOYS IN ORES, ROCKS, AND OTHER MATERIALS

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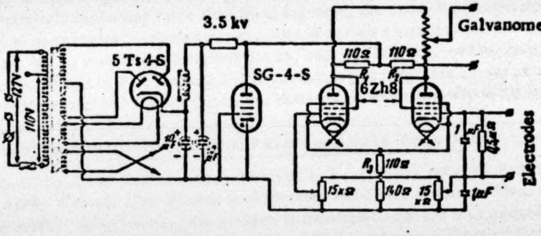
Hitherto no papers have been published which deal with the potentiometric micro-titration of manganese. Potentiometric macro-titration of manganese using bimetallic electrodes [1-3], and methods suggested by other authors [4, 5], have not found wide application for a variety of reasons. In 1946 Lingane and Karplus [6] showed that it is possible to get good results during potentiometric titration of divalent manganese to the trivalent state using a solution of potassium permanganate in a pyrophosphate medium at pH 3-7. Numerous metals did not interfere as long as they were oxidized to a higher valency state. This method was subsequently improved by Busev [7], Busev and Dmitrieva [8, 9], and later by Kreimer [10], who increased the sensitivity of the method. Large amounts of vanadium interfere.

In order to increase the sensitivity of the method ten times and for ensuring the possibility of titrating micro-gram amounts of manganese, we used a highly sensitive setup for potentiometric titration and torsion micro-balances type VT-20 produced by the Tekstilpribor factory which have a high sensitivity.



Schematic diagram of the tube potentiometer

A schematic diagram of the tube potentiometer used is shown above. The apparatus operates on the lighting circuit with a voltage of 110-127 volt and is connected with the electrodes and with an M-122 galvanometer. The output potential after passing through a transformer, a 5 Ts-4S kenatron, a capacitance, and an SG-4-SO stabilizer is applied to the anodes of two pentodes 6Zh-8, connected in bridge fashion. By changing the variable resistance in the arm it is possible to alter over wide limits, both the overall sensitivity of the apparatus, as well as the position of the needle on the scale of the M-122 galvanometer *.

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* Similar setups have been described in the literature [11], and can be assembled from ordinary components.

The construction of the stand and stirrer with rotating platinum electrode enables one to change the solution easily by lifting and lowering electrode and motor and fixing the movable part of the stirrer-stand combination with a screw. The speed of rotation of the motor was kept constant by means of a voltage stabilizer and a LATR-2 autotransformer.

The torsion micro-balance which we used differed from the industrial type VT-20 torsion balance produced by the Tekstilpribor factory in that the one we used was five times more sensitive. This was achieved by using a specially constructed scale (made to order) which was subdivided into 1000 divisions (instead of 200 divisions), and the use of two supplementary lenses 4^+; one of which was movable and shifted with the balance indicator. Accuracy of weighing was ±0.01 mg. The effect of temperature on weighing was less than when a type VM-20 micro-balance was used. One weighing operation took 1-2 minutes on a VT-No3422 balance. 5 and 10 mg standard weights were supplied with the balance. The balance is completely suitable for weighing samples during micro-analytical determinations.

Special Features in Manganese Determination

Manganese can be determined by potentiometric titration either on the macro- or micro-scale. The micro method is more rapid and requires considerably less reagents; it can be used in all cases where there is no doubt about the homogeneity of test samples, and where samples have been chosen according to correct sampling procedures. Using a micro technique, manganese in amounts of hundredths of a percent can be determined. The sensitivity can be increased to cover thousandths and ten thousandths of a percent by increasing sample weight to 0.2 and 2.0 g. Aliquots of this size are taken during analysis of pure metals, alloys, and other metals with low manganese contents.

Test solution should contain nitric and hydrochloric acids. Nitric acid is included for the purpose of oxidizing other metals which are present to higher valency states. Chloride ions should be present in order to reduce permanganate and manganate to divalent manganese. Sample aliquots can be broken down in other acids or mixtures of other acids, e.g. sulfuric, hydrochloric acid, etc. Excess acid is removed by evaporation, and the necessary amounts of nitric and hydrochloric acid introduced. During potentiometric micro determination of up to 2% manganese, the strength of the permanganate solution should be 0.001 N, while for determination of materials containing more than 2% manganese, the strength of the permanganate used should be 0.01 N. The 0.01 N permanganate solution is standardized against a standard sample containing a high percentage of manganese but no vanadium. Standards SO 35, 163, and 201, etc. can be used. During micro determinations, one drop (0.025 ml) of 0.01 N and 0.001 N potassium permanganate causes an appreciable shift in the galvanometer needle at the equivalence point; this corresponds approximately to 10 and 1 γ of Mn.

Standardization of Potassium Permanganate Solution

15-20 mg of standard sample is dissolved in a mixture of concentrated nitric acid – 8 drops – and hydrochloric acid – 8 drops. The solution is evaporated and 15 ml of water added, the solution is boiled to expel nitrogen oxides. After cooling, the solution is transferred to a 250 ml standard flask and diluted to the mark with water; the flask is shaken up thoroughly. 25 ml of this solution is pipetted into a 100 ml beaker containing 50 ml of 10% sodium pyrophosphate solution, and the rotating platinum electrode (kept beforehand for 1-2 minutes in concentrated sulfuric acid and washed with water) lowered into it. Concentrated sulfuric acid (or 25% ammonia solution) is added dropwise until blue litmus paper 2-3 mm wide acquires a weak rose color on dipping it in the solution (pH 5-7). Excess acid or alkali is detetrimental to the determination.

A saturated calomel electrode is lowered into the solution and the galvanometer needle moved to the left hand side of the scale by manual adjustment of the tube potentiometer; the needle should not touch the arresting device. 0.01 N potassium permangante is added dropwise from a micro-buret (with scale divisions of 0.01 ml) until the galvanometer needle moves strongly to the right. The rate at which the permanganate is added is then slowed down considerably – towards the end point the rate of addition should be about 1 drop per minute. The equivalence point is taken as that point at which, after addition of one drop, the galvanometer needle does not return for one minute to its initial position after being deflected to the right arresting device on addition of that drop, but stays by the arresting device for that minute.

0.001 N potassium permanganate was standardized the same way as 0.01 N permanganate; in the case of the former however the solution of the aliquot was diluted in a two liter standard flask and 20 ml solution taken for titration. Before each titration with 0.001 N permanganate it is necessary to wash the rotating platinum electrode in concentrated sulfuric acid and then in water. The low stability of 0.001 N potassium permanganate necessitates daily standardization. The 0.01 N solution is standardized once every three days.

Determination of Manganese in Steels, Casts, and Non-Ferrous Metals and Alloys Containing up to 2% Mn

15-20 mg is dissolved in 8 drops each of concentrated nitric acid and 8 drops of hydrochloric acid in a 100 ml beaker. High chromium steels, alloy steel, and casts are dissolved in the minimum amount of dilute sulfuric acid 1:4. The solution is evaporated and after removal of excess acid, the same amounts of nitric and hydrochloric acids are added (8 drops each). The solution is then evaporated again and 1-2 drops of concentrated nitric acid added in order to oxidize carbides (until foaming stops). Approximately 15 ml of water is added and the solution boiled in order to expel nitrogen oxides. After cooling, 50 ml of 10% sodium pyrophosphate is added and the solution adjusted to the required acidity; it is finally titrated with 0.001 N potassium permanganate using the technique described above for standardization.

Manganese in amounts of thousandths and ten thousandths of a percent is determined on aliquots of 0.2 and 2 g, using larger amounts of sodium pyrophosphate in a 400 ml beaker, and 0.001 N potassium permanganate.

When manganese is determined in magnesium alloys, during transfer of the solution after dissolving the aliquot in 10% sodium pyrophosphate, an insoluble, white coagulated precipitate readily falls out. Consequently, it is best to carry out determination of manganese in magnesium alloys on micro amounts. When a macro method is used, determination of manganese can be carried out after taking an aliquot part of the solution corresponding to a micro amount of original sample.

Determination of Manganese in Manganese Ores, Agglomerates, Ferromanganese, and Other Materials Containing more than 2% Mn

15-20 mg of ore, agglomerate, or ferromanganese is dissolved as described above in a mixture of hydrochloric and nitric acids. 15 ml of water is added and the mixture boiled; the solution is transferred to a 250 ml standard flask, in which it is diluted to the mark and thoroughly mixed. 25 ml of solution is taken for titration and is transferred to a 100 ml beaker containing 50 ml of 10% sodium pyrophosphate. The acidity of the solution is adjusted to the required value and is titrated with 0.01 N potassium permangante.

Determination of Manganese in Slags, Rocks, and Silicates

Determination of manganese in slags, rocks and silicates can be carried out as usual either by macro or micro techniques, after dissolving the test aliquot.

Results of manganese determination using micro amounts of 15-20 mg are given in the Table.

Standard sample No.	Material tested (sample weight 15-20 mg)	Specified content, in %	Content as determined by potentiometric titration, in %
5-V	Dynamo steel	0.18	0.18; 0.19; 0.18; 0.16
84-G	Rail steel, Bessemer	0.72	0.73; 0.72; 0.72; 0.72
109-a	Chromium-manganese-silicon steel	1.00	1.01; 1.01; 1.01; 1.01; 1.01
117	Steel	1.48	1.47; 1.48; 1.48; 1.47
35	Ferromanganese	74.90	75.0; 75.0; 75.0; 74.7
163	″	87.79	87.6; 87.9; 87.9
201	″	92.40	92.14; 92.24; 93.14
44	Manganese ore	52.58	52.61; 52.53
68-a	Aluminum-iron-manganese-bronze	1.49	1.50; 1.49; 1.50
69-a	Dural	0.61	0.60; 0.61; 0.67
60	Nikitinsky Dolomite	0.23	0.24; 0.23
82	Magnesite brick, Satinsky	0.044	0.050; 0.036

SUMMARY

Potentiometric titration of small amounts (micro gram amounts) of manganese can be carried out with satisfactory accuracy in a weakly acid pyrophosphate medium, using potassium permanganate as titrant, and sample aliquots of 15-20 mg.

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PHOTOMETRIC DETERMINATION OF COBALT WITH PYRAZOLONE DERIVATIVES

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Many of the gravimetric and titrimetric methods which have been described for determination of cobalt are complicated and are difficult to carry out. Small amounts of cobalt are determined photometrically as $[Co(SCN)_4]^{2-}$; when this method is used excess thiocyanate is required as well as the use of an organic solvent for extracting the complex compound formed.

Gusev has shown that under certain conditions, pyramidone, a derivative of pyrazolone forms with Co^{2+} and SCN^- in acid media, a compound $(C_{13}H_{17}ON_3)_2\,H_2[Co(SCN)_4]$ [1]. The author however did not develop a qualitative reaction for cobalt based on this reagent, nor a quantitative method of determining this metal. Zhivopistsev [2] has described a spot reaction for cobalt using diantipyrylmethane.

We have established that it is possible to extract the compound formed $[C_{11}H_{11}ON_2)_2CH_2]_2H_2[Co(SCN)_4]$ by means of chloroform and some other organic solvents to give a blue extract.

Diantipyrylmethane derivatives also react with the anion $[Co(SCN)_4]^{2-}$ to form precipitates which dissolve readily in chloroform, benzene, and other solvents to give a blue color. The intensity of the color developed is proportional to the amount of cobalt in solution, so that it is possible to develop a method for photometric determination of cobalt. Fe^{3+}, Cr^{3+}, Cu^{2+}, V^V, Mo^{VI}, Ti^{3+}, Ni^{2+} and W^{VI} interfere with the photometric determination of cobalt.

In the presence of iron, nickel, and quinquevalent vanadium, cobalt can be determined quantitatively after preliminary reduction of iron to the ferrous state with ascorbic acid, and addition of ammonium acetate and tartaric acid to the solution [3]. The nickel complex which is green is not extracted by benzene.

Synthesis of Diantipyrylmethane and Its Derivatives. Diantipyrylmethane was synthesized from antipyrine and formaldehyde [4]; diantipyrylmethylmethane was synthesized from antipyrine and acetaldehyde [5]. Diantipyrylpropylmethane was obtained from antipyrine and butyraldehyde as well as diantipyrylmethylmethane. Diantipyrylphenylmethane was synthesized from antipyrine and benzaldehyde [6]. Diantipyryl-p-tolyl methane was synthesized, by analogy with the previous compounds, from antipyrine and p-tolyl aldehyde in the presence of concentrated HCl. The material dissolves readily in alcohol, acetic acid; it is crystallized in the form of needles from dilute alcohol and melts at 128-130°. This is the first time that it has been prepared. Diantipyryl-ortho-hydroxy-and p-hydroxyphenylmethanes were obtained from the corresponding salicaldehydes and antipyrine [7]. Diantipyryl-o-nitrophenyl methane was synthesized from antipyrine and o-nitrobenzaldehyde [8]. Diantipyryl-p-dimethylaminophenylmethane was obtained from antipyrine and p-dimethylaminobenzaldehyde [9].

Synthesis of Complex Compounds of Cobalt with Diantipyrylmethane and its Derivatives. Complex compounds of cobalt with diantipyrylmethane and its derivatives, respectively, and thiocyanate, were prepared by the interaction of equivalent amounts of cobalt salts, ammonium thiocyanate, and reagent in the presence of hydrochloric acid.

The complex formed between cobalt, diantipyrylmethane, and the thiocyanate ion was prepared as follows: 0.776 g of diantipyrylmethante (0.002 mole), 0.24 g of $CoCl_2 \cdot 6H_2O$ (0.001 mole) and 0.3 g of ammonium thiocyanate (0.004 mole), were dissolved in alcohol and acidified with 2N hydrochloric acid to give an acid

TABLE 1

Some Properties and Analytical Results of Cobalt Complexes

Formula	Solvent used for recrystallization	Crystal form	Melting point in deg.	Co found in %	Co Calculated, %	SCN found, %	SCN calculated, in %	H+ found in %	H+ calculated, in %
$[(C_{11}H_{11}ON_2)_2CH_2]_2H_2[Co(SCN)_4]$	Ethyl acetoacetate	Needles	156—158	5.32	5.50	22.2	21.71	—	—
$[(C_{11}H_{11}ON_2)_2CHCH_3]_2H_2[Co(SCN)_4]$	Ethyl acetoacetate	Fine needles	110—112	5.14	5.36	—	—	0.16	0.18
$[(C_{11}H_{11}ON_2)_2CHC_3H_7]_2H_2[Co(SCN)_4]$	Acetone	Plates or needles	127—129	5.23	5.11	19.57	20.12	0.178	0.173
$[(C_{11}H_{11}ON_2)_2CHC_6H_5]_2H_2[Co(SCN)_4]$	Ethyl acetoacetate	Clusters of needles	185	4.71	4.82	—	—	0.137	0.167
$[(C_{11}H_{11}ON_2)_2CHC_6H_4CH_3]_2H_2[Co(SCN)_4]$	Ethanol	Rods	153—156	4.72	4.71	18.14	18.58	—	—
$[(C_{11}H_{11}ON_2)_2CHC_6H_4OH\text{-}o]_2H_2[Co(SCN)_4]$	Ethyl acetate	Plates	198—200	4.49	4.69	19.1	18.52	—	—
$[(C_{11}H_{11}ON_2)_2CHC_6H_4OH\text{-}n]_2H_2[Co(SCN)_4]$	Ethyl acetoacetate	Needles	170—172	4.73	4.69	18.52	18.52	—	—
$(C_{11}H_{11}ON_2)_2CHC_6H_4NO_2]_2H_2[Co(SCN)_4]$	Alcohol	Plates	Sublimates above 150°	4.71	4.49	—	—	0.153	0.152

TABLE 1

reaction to Congo Red. A blue precipitate separated out which was separated as usual.

Cobalt complexes with diantipyryl-,propyl-, phenyl-,tolyl-, o-hydroxyphenyl-, p-hydroxyphenyl-, o-nitrophenyl-, and p-dimethylaminophenylmethane respectively, and thiocyanate ions were synthesized in a similar way (Table 1); they are crystalline materials with a bright blue or blue color, insoluble in water, but soluble on heating in alcohol, ethyl acetoacetate; they are readily soluble in acetone and chloroform.

The SCN^- content of the compounds obtained was determined as $Cu_2(SCN)_2$, the cobalt was determined as $CoSO_4$ and the hydrogen ion by titration.

The hydrogen ion content was determined by dissolving the test compound in alcohol on heating, and diluting the solution obtained with water until the blue color of the solution changed to rose; the final solution was titrated with 0.05 N NaOH in the presence of Tashir indicator [10]. Analytical results are given in Table 1.

Conditions for Carrying out the Reaction between $CoCl_2$ and Diantipyrylmethane or its Derivatives. In order to establish the optimum conditions for carrying out the reaction between cobalt and diantipyrylmethane or its derivatives, and thiocyanate, the requisite amounts of acid, reagent, and ammonium thiocyanate were determined by comparing the intensity of the color of solutions during extraction of the blue precipitate with chloroform.

Preparation of a Standard Solution of Cobalt Salt. 0.1 g of cobalt metal was dissolved in 5 ml of concentrated hydrochloric acid (sp.gr. 1.19) in a 200 ml standard flask. The solution obtained was diluted to the mark with water. 10 ml of this solution was transferred in turn to a 100 ml standard flask and again made up to the mark with water. This solution contained 0.05 mg/ml of Co. The cobalt concentration of this solution was determined by means of α-nitroso-β-naphthol suggested by Ilinsky [11].

In order to establish the optimum conditions for carrying out the reaction between diantipyrylmethane with $CoCl_2$ the following tests were carried out: to 2 ml lots of a solution of cobalt salt containing 0.05 mg/ml of Co, contained in a series of test tubes, were added 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; and 0.7 ml of saturated NH_4SCN solution, 0.5 ml of 0.1 N H_2SO_4, 0.5 ml of 1% reagent solution and 2 ml chloroform. It was established that the color of the chloroform extract is brightest when 0.5 ml of saturated NH_4SCN was used.

The color of the chloroform layer was most intense, other conditions being the same (0.5 ml of saturated NH_4SCN, 0.5 ml of 1% reagent solution etc) when 1 ml of 0.1 N sulfuric acid was used. The amount of reagent required was found by taking a series of test tubes and introducing into each of them 2 ml of $CoCl_2$ of the concentration indicated, 0.5 ml of saturated NH_4SCN solution, 1 ml of 0.1 N H_2SO_4, and 2 ml of chloroform; the amount of 1% reagent solution used was varied from 0.5 to 2 ml. Optimum results were obtained on using 1 ml of a 1% solution of diantipyrylmethane. Optimum conditions for the use of the other derivatives of this reagent were established in the same way. Results are given in Table 2.

TABLE 2

Optimum Conditions for Carrying out the Reaction

Reagent	Saturated NH_4SCN solution ml	0.1 N H_2SO_4, in ml	% Reagent solution, ml	Water ml	$CHCl_3$
Diantipyrylmethane	0.5	1.0	1.0	—	2
Diantipyrylmethylmethane	0.5	1.0	1.0	1.5	2
Diantipyrylpropylmethane	0.5	0.5	1.0	—	2
Diantipyrylphenylmethane	0.5	1.0	1.5	4.5	2
Diantipyryltolylmethane	0.5	0.5	1.0	4.5	2
Diantipyryl-o-hydroxyphenylmethane	0.5	1.0	2.0	4.0	2
Diantipyryl-p-hydroxyphenylmethane	0.5	1.0	1.0	—	2
Diantipyryl-o-nitrophenylmethane	0.5	1.0	0.8	—	2
Diantipyryldimethyl-p-aminophenylmethane	0.5	0.5	1.5	—	2

It follows from the results given in Table 2 that during cobalt determination with diantipyrylpropylmethane, diantipyryltolylmethane, and diantipyryldimethylaminophenylmethane, the acidity must be lower than when the other reagents are used. The amount of reagent which must be used varies from 0.8 to 2 ml. The amount of ammonium thiocyanate solution is the same in each instance under the conditions used. Water was only added in four instances – 2,4,5, and 6 – for eliminating turbidity during extraction with chloroform; in the remaining cases the extracts were transparent without addition of water; excess of the latter can lead to decomposition of the dissolved complexes.

TABLE 3

Sensitivity of the Reactions of $CoCl_2$ with Diantipyrylmethane and Its Derivatives

Reagent	Sensitivity, as Co γ/ml
Diantipyrylmethane	7.5
Diantipyrylmethylmethane	7.5
Diantipyryl-o-hydroxyphenylmethane	7.5
Diantipyryl-p-hydroxyphenylmethane	7.5
Diantipyrylpropylmethane	10.0
Diantipyryltolylmethane	10.0
Diantipyrylphenylmethane	15.0
Diantipyryl-p-nitrophenylmethane	15.0
Diantipyryl-p-dimethylaminophenylmethane	20.0

The sensitivity of the reaction was established as follows: a standard cobalt salt solution (prepared as described above) was diluted so that its cobalt content was 0.05 γ/ml. To a known volume of this solution was added the appropriate amounts of reagents (the optimum amounts given in Table 2) and 1 ml of chloroform. Results are given in Table 3.

These results show that the sensitivity of the reactions with diantipyrylmethane, diantipyrylmethylmethane, diantipyryl-p-hydroxyphenylmethane, and diantipyryl-o-hydroxyphenylmethane respectively is the same and is greater than in the cases of the other derivatives.

Quantitative Determination of Cobalt in $CoCl_2$. Into a 50 ml separating funnel was introduced various amounts of $CoCl_2$ solution (2, 1.8, 1.6, 1.4, and 1.2 ml); to the aliquot was added 0.5 ml of saturated NH_4SCN solution, 0.1 N H_2SO_4, and an alcoholic solution of reagent. A blue precipitate separated out which was extracted with chloroform. The chloroform layer was then transferred to a beaker prior to colorimetric measurements.

The concentration of one of the solutions obtained was taken as a standard, and the solution obtained from the 2 ml aliquot compared with the solution obtained from the 1.8 ml aliquot; the 1.8 ml solution with the 1.6 ml solution, etc. The instrument used for analysis was Colorimeter-Nephelometer Type No.235 made by the "Krasnogvardeets" factory. Results for cobalt determinations are given in Table 4.

TABLE 4

Determination of Cobalt in $CoCl_2$ Solution

Reagent	Co, in mg		Relative error, in %
	taken	found	
Diantipyrylmethane	0.09	0.089	− 1.1
Diantipyrylmethylmethane	0.085	0.083	− 2.4
Diantipyrylpropylmethane	0.070	0.071	+ 1.4
Diantipyrylphenylmethane	0.085	0.078	− 7.8
Diantipyryl-o-hydroxyphenylmethane	0.085	0.081	− 4.7
Diantipyryl-p-hydroxyphenylmethane	0.070	0.0702	+ 0.3
Diantipyrylnitrophenylmethane	0.060	0.063	+ 5.0
Diantipyryldimethyl-p-aminophenylmethane	0.090	0.091	+ 1.1
Diantipyryltolylmethane	0.085	0.083	− 2.4

These results show that the experimental error lies within acceptable limits. Next we determined cobalt in aluminum-iron-manganese bronze containing Cu –86%, Al –8.7%, Fe –2.6%, Mn –1.5%, and also in cast iron.

Quantitative Determination of Cobalt in Bronze. 0.1 g of bronze was dissolved in 2 ml of HNO_3 (1:1) in a 100 ml standard flask. The solution was made up to the mark with distilled water; to 2 ml of this solution was added 2 ml of $CoCl_2$ containing 0.05 mg Co/ml, a few drops of NH_4OH (1 N) for neutralization, 1.0 ml of $Na_2S_2O_3$ (1.0 N) for complexing iron and copper, 0.5 ml of saturated NH_4SCN solution, 1-2 ml of the appropriate reagent, 0.1 N H_2SO_4, and 2 ml chloroform. The blue chloroform solution was transferred to a beaker for colorometric measurements. 2 ml of $CoCl_2$ solution containing 0.1 mg of Co was taken as a standard; to this was added 2 ml of distilled water, 1-2 drops of 1.0 N NH_4OH for neutralization, and the remaining reagents in the quantities given above for analysis of bronze to which $CoCl_2$ has been added.

The results given in Table 5 show that cobalt can be determined quantitatively in the presence of copper, iron, manganese, zinc, and aluminum.

Determination of Cobalt in Cast Iron. 0.1 g cast iron was dissolved in 7 ml HCl (sp.gr. 1.19) and 2 ml HNO_3 (sp.gr. 1.14). The solution was evaporated until salts crystallized out. The dry residue was moistened with 5 drops of HCl (sp.gr. 1.19) and diluted with 5 ml of water; this mixture was evaporated to give a residual volume of 2 ml. On cooling, 1 g of NH_4Cl and 10 ml of distilled water were added and the solution neutralized with NH_4OH (1:1), until ferric hydroxide separated out; the latter was dissolved in 1-2 drops of HCl (1:1) [12]. Solution of cast iron was transferred to a 100 ml standard flask and its volume made up to the mark with water; the solution was filtered into a dry flask through a dry filter; 4 ml of the filtrate obtained was transferred to a 50 ml flask with a ground stopper, and 4 ml of ascorbic acid solution added to it in order to reduce the iron from Fe^{3+} to Fe^{2+}; the solution was neutralized with a few drops of 1 N NH_4OH; to the solution was then added 1 ml of 0.1 N H_2SO_4, 4 ml of saturated NH_4SCN solution, 1 ml of a 70% CH_3COONH_4 solution, and 1 drop of 50% tartaric acid for eliminating interference from vanadium. The blue precipitate was extracted with chloroform. The extract was then measured colorometrically. The standard taken was 4 ml of $CoCl_2$ solution containing 0.025 mg Co/ml, to which was added the same amounts of the respective reagents as were used for the analysis. During colorimetric determination of cobalt in cast using diantipyrylmethane and diantipyryl-p-nitrophenylmethane as reagents respectively, another variant was worked out, in which iron was complexed with sodium pyrophosphate, while benzene was used as solvent.

The amount of sulfuric acid necessary for neutralizing cast iron solutions and standard solution was determined in preliminary experiments using Methyl Orange as indicator.

TABLE 5

Determination of Cobalt in Bronze (Containing 0.100 mg of Co in the Aliquot of Alloy taken)

Reagent	Co found, in mg	Relative error, %
Diantipyrylmethane	0.100	—
Diantipyrylmethylmethane	0.100	—
Diantipyrylpropylmethane	0.093	— 7.7
Diantipyryltolylmethane	0.102	+ 1.7
Diantipyrylphenylmethane	0.107	+ 7.0
Diantipyryl-o-hydroxyphenylmethane	0.096	— 4.0
Diantipyryl-p-hydroxyphenylmethane	0.103	+ 3.0
Diantipyryl-o-nitrophenylmethane	0.096	— 4.0
Diantipyryldimethyl-p-aminophenylmethane	0.110	+10.0

TABLE 6

Determination of Cobalt in Iron (Containing 0.100 mg Co in the Aliquot taken)

Reagent	Co found in mg	Relative error, in %
Diantipyrylmethane	0.105	+ 5.0
Diantipyrylmethylmethane	0.102	+ 2.0
Diantipyrylpropylmethane	0.098	— 2.0
Diantipyrylphenylmethane	0.101	+ 1.0
Diantipyryl-p-tolylmethane	0.095	— 5.0
Diantipyryl-o-hydroxyphenylmethane	0.101	+ 1.0
Diantipyryl-p-hydroxyphenylmethane	0.101	+ 1.0
Diantipyryl-p-nitrophenylmethane	0.101	+ 1.0
Diantipyryldimethyl-p-aminophenylmethane	0.099	— 1.0

4 ml of the iron solution was transferred to a 50 ml separating funnel; to this aliquot was added 4 drops of a saturated solution of ammonium thiocyanate, 2 ml of 10% $Na_4P_2O_7$, 5.2 ml of 0.1 N H_2SO_4, and 1 ml of a 1% solution of diantipyrylmethane. The precipitate which separated out was extracted with 5 ml of benzene on vigorous shaking. After 20 minutes the benzene layer was colorimetrically measured.

Colorimetric determination of cobalt in solutions of cast using diantipyryl-o-nitrophenylmethane was carried out in the same way, except that 1.5 ml of pyrophosphate solution was added, while the amounts of reagent solution and saturated ammonium thiocyanate solution used were 0.8 ml and 5 drops respectively.

Results of cobalt determination are given in Table 6.

SUMMARY

1) Complex compounds formed between cobalt, thiocyanate ions, and diantipyrylmethane and its derivatives (methyl-, propyl-, phenyl-, p-tolyl-, p-and o-hydroxyphenyl, and dimethyl-p-aminophenyl) have been prepared.

2) Diantipyryl-p-tolylmethane has been used for analysis for the first time.

3) A colorimetric method in which diantipyrylmethane and its derivatives are used as reagents is suggested for determination of cobalt in some alloys.

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PHOTOMETRIC DETERMINATION OF BORON IN STEEL

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The normal methods used for determining boron in steels usually involve distillation of the former as methyl borate [1-3], or preliminary removal of heavy metals as hydroxides [2]. These methods are long and are not suitable for determination of microgram amounts of boron. Attempts to reduce the ferric ion – ferric ions in particular, interfere with boron determination – by using hydroxylamine, hydrazine, and other reducing agents have not led to good results [4]. Taking into account the necessity of developing a reliable method of determining more than 0.001% of boron, we tested many reagents suggested for this purpose [5-11], and as a result of our studies became convinced that many of these reagents only give satisfactory results when they are used for determining boron in solutions free from other materials; all of them however proved to be unsuitable in the presence of iron ions. Accordingly, in order to solve the problem it is necessary either to find a method of removing iron whereby it would be possible to determine boron subsequently, or to find reagents which would allow boron to be determined in a solution of steel.

The present article contains a description of a method involving carmine whereby boron can be determined in the presence of iron.

F. P. Zorin [12] was the first to suggest carmine for the qualititative detection of boron. V. A. Kazarinova-Okn!na [13] has developed a procedure for determining boron in rocks. Recently, carmine was suggested for determining boron in materials used for uranium reagents [14]. The question of the influence of iron under such conditions has not been investigated.

Since boron as accidental contamination may be found not only in reagents, but also in glass apparatus and water, in order to eliminate possible errors we carried out a systematic check on the presence of boron by the reaction with turmeric paper which was prepared according to Petrashen's method [15]. Tests were made using Faigl's method [16], in which the limit of identification is 0.02 γ of boron. The dry reagents were freed from boron by recrystallization. Concentrated sulfuric and phosphoric acids were given a preliminary boiling for 10 minutes in a platinum crucible. The 30% hydrogen peroxide solution was checked for boron after preliminary oxidation with $KMnO_4$. The distilled water used was twice distilled. Steel was brought into solution in a flask of quartz glass. Additional operations were carried out for the most part in the same apparatus made of normal laboratory glass "Druzhnaya Gorka" type, since replicates in this apparatus and in the quartz flask gave practically identical results.

Steel samples were tested beforehand for boron by the turmeric reaction; in addition, the intensity of solutions colored by carmine and prepared from pure water was photocolorimetrically compared with solutions prepared from steel.

The first experiments were carried out in order to establish the possibility of determining boron in solutions whose composition corresponds to those of solutions obtained on dissolving carbon steel. To 2.00 ml of the boron solution in a 25 ml standard flask was added 10 ml of concentrated H_2SO_4. The contents of the flask were cooled and 10.00 ml of 0.05% solution of carmine added; the solution was made up to the mark with concentrated H_3PO_4 and the whole thoroughly mixed. The intensity of the color developed was measured on an FEK-M photocolorimeter, using as a standard a solution prepared from distilled water under identical conditions. A 5 cm cell was used in conjunction with a green filter, since the absorption maximum of the colored compound lies at 620 mμ.

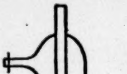
Each point on the calibration curve was obtained by averaging the results of four independent experiments. Boron was subsequently determined in the presence of various amounts of Fe^{3+} ions. The results of these experiments, which are given in Table 1, show that Fe^{3+} ions do not interfere when boron is determined by means of carmine. The next group of experiments on determination of boron, in which various amounts of boron were added to solutions of carbon steel, gave similar results. It was established however that the calibration curve constructed for solutions of boron in carbon steel differed slightly from the curve obtained for aqueous solutions; accordingly in the course of subsequent analyses we used curves which corresponded to the test sample.

TABLE 1

Determination of Boron in the Presence of Various Amounts of Iron (in a volume of 25 ml)

Boron taken, in γ	Fe^{3+} added, in g	Boron found, in γ	s^2	$s_{\bar{x}}$	$t_{0.95}\cdot s_{\bar{x}} - B$
1.00	0.01—0.05	1.05; 0.85: 1.15; 0.95	$1.8\cdot10^{-2}$	$6.8\cdot10^{-2}$	0.21
1.50	0.01—0.05	1.54; 1.42; 1.55; 1.48	$0.39\cdot10^{-2}$	$3\cdot10^{-2}$	0.10
3.00	0.01—0.05	3.00; 2.95; 2.98; 3.05	$0.18\cdot10^{-2}$	$3.7\cdot10^{-2}$	0.12
5.00	0.01—0.05	5.15; 5.00; 4.68; 4.96	$3.1\cdot10^{-2}$	$8.7\cdot10^{-2}$	0.27

In order to determine loss of boron during solution of steel the following tests were carried out: to a 0.5 g aliquot of steel free from boron contained in a 150 ml quartz flask (Fig.1) were added known amounts of a boron solution, and 25 ml H_2SO_4 (1:4); the flask was connected to a reflux condenser cooled with tap water, and the steel dissolved on gentle warming. When the steel had dissolved completely, 2 ml of 30% hydrogen peroxide was added through the top of the condenser, and the heating was continued until carbides had been destroyed and excess hydrogen peroxide had ben destroyed. With the condenser still in position the flask was cooled, and the condenser rinsed with a few ml of distilled water. The solution obtained was diluted to the mark in a 50 .0 ml standard flask and the whole thoroughly mixed. 2.5 ml of this solution was taken for boron determination, subsequent procedure being the same as that described already. Preliminary tests showed that under these conditions, there was always some residual hydrogen peroxide left in the solution; in order to destroy it, 0.1 N $KMnO_4$ solution was added dropwise to the solution after disconnecting the flask from the condenser until the pink color of the permanganate did not disappear; excess $FeSO_4$ solution was added in sufficient amount to reduce the former completely.



Apparatus for Dissolving Steel.
Condenser 1 and funnel 2 are fused into the bottom of a hollow glass stopper 3 which fits to flask 4 with a capacity of 150 ml.

Solutions containing more than 0.05 g Fe^{3+} per 25 ml of the final sulfuric acid solution became turbid 1-2 hours after preparation. When Cr^{3+} and Ni^{2+} ions were present, the solution became turbid as soon as H_2SO_4 was added. Since it was found that filtered solution also became turbid because separation of solid phase is a time reaction, attempts were made to prevent this by adding phosphoric acid; in the presence of the latter $FeHPO_4{}^+$ ions are formed which have an instability constant of 4.4 × 10^{-10} [17].

In all probability, under these conditions, Cr^{3+} ions are partially, if not completely, complexed as a phosphate complex in the same way as Fe^{3+} ions.

The method was checked by dissolving 1 g of steel in 10 ml of H_2SO_4 (1:4). After destruction of carbides and oxidation of iron, 2.5 ml of concentrated H_3PO_4 was added to the contents of the flask and heating was continued to effect breakdown of excess H_2O_2. $KMnO_4$ was used to clear up traces of H_2O_2 left; the solution was then transferred to a 25 ml standard flask where the volume was made up to the mark with water. 2.5 ml of the transparent solution was used for boron determination; this aliquot was transferred to a 25 ml flask and the procedure described previously followed. Solutions prepared in this way remained completely transparent for 8 hours when they contained 0.1 g of Fe^{3+} as against 0.05 g before. It should be noted that when the experiments were carried out, the same amounts of original solutions were taken as before, so that possible errors introduced as a result of the presence of very small amounts of boron remaining as impurity after purification, compensate in each case for the presence of exactly the same amounts of boron in the standard solution with which the test colored solutions were compared. The results which are given in Table 2 show that in the presence of H_3PO_4, boron can be determined by means of carmine in the presence of steel, without preliminary separation of heavy metals.

TABLE 2

Determination of Boron in Steels (the amounts of boron refer to 1 g of steel)

Mark of Steel	Boron added, in γ	Boron found, in γ	No. of expts.	s^2	$s_{\bar{x}}$	$t_{0.95} \cdot s_{\bar{x}} = \varepsilon$
Carbon	10	10.2	7	1.48	0.47	1.10
	20	20.4	7	1.04	0.39	0.90
	30	30.2	7	1.96	0.53	1.19
	40	39.2	7	1.24	0.40	1.00
Chrome-nickel	15	15.1	5	1.02	0.46	1.20
	40	39.7	5	1.02	0.43	1.00
	60	59.7	5	5.00	1.0	2.78

Mathematical treatment of the results [18], which is also included in Table 2, shows that at a confidence level of $\alpha = 0.95$, the relative experimental error does not exceed 11%.

The last three columns of both Tables 1 and 2 contain the results of statistical analysis of the experimental results obtained. Here s^2, which is the dispersion, was calculated by means of the formula $s^2 = \frac{\Sigma(x_i - \bar{x})}{n-1}$, where n is the number of measurements; x_i is the result of individual measurments; $\bar{x}$ is the arithmetic mean; $s_{\bar{x}}$ is the standard arithmetic mean calculated from the formula $s_{\bar{x}} = \frac{s}{\sqrt{n}}$ and, finally, $\varepsilon_{0.95}$ is the accuracy which was calculated from the formula $\varepsilon_{0.95} = t_{0.95} \cdot s_{\bar{x}}$, where the significance is $t_{0.95}$, for which the probability $P(-t_{0.95} < t < t_{0.95}) = \alpha$ [19].

EXPERIMENTAL PROCEDURE

1 g of steel is dissolved in 10 ml sulfuric acid 1:4 contained in a 150 ml quartz flask fitted with a reflux condenser; 4 ml of 30% H_2O_2 was then introduced through the dropping funnel fitted into the same stopper alongside the reflux condenser (diagram), and the solution boiled until it becomes clear and carbides are decomposed. 2.5 ml of concentrated H_3PO_4 is then added through this same funnel and heating continued for 20-30 minutes to destroy excess hydrogen peroxide. The flask is cooled without removal of the reflux condenser, and the latter washed with 5 ml of cold distilled water; the condenser is disconnected from the flask and 0.1 N $KMnO_4$ added dropwise until the solution acquires a permanent pink color (usually 2-3 drops); the whole is thoroughly mixed and excess $KMnO_4$ removed by addition of a few drops of 0.1 N $FeSO_4$. The solution is transferred to a 25 ml standard flask where it is made up to the mark with distilled water; it is shaken again and then filtered through a dry filter paper. The first 3-5 ml are discarded and filtration continued into a dry clean flask; 2.5 ml of the solution obtained is transferred to another 25 ml standard flask and 10 ml of concentrated H_2SO_4 added, the mixture being rapidly cooled with cold water. 10.00 ml of a 0.05% carmine solution in concentrated sulfuric acid is added next and the solution made up to the mark with concentrated sulfuric acid; this final solution is also shaken thoroughly. The solution is measured photometrically after 1 hour using 3-5 cm cells and a green filter. A blank is carried out in exactly the same way using a solution prepared from steel free from boron but whose content of the other metals is the same as that of the test steel. When such steel is not available, a blank can be prepared from carbon steel free from boron by adding the necessary elements in the appropriate amounts to the solution. An even simpler procedure is to use the solution of test steel after removal of the boron from it as methyl borate. This is carried out as follows: 1 g of steel is placed in a flask, 10 ml of distilled water, 10 ml H_2SO_4 (1:4), and 2.5 ml of H_3PO_4 are added and the steel dissolved on gentle warming. When solution is complete 4 ml of 30% H_2O_2 is added dropwise and the whole boiled and then evaporated to a low volume. 10 ml of

methanol is added to the solution obtained and the mixture obtained boiled until the original volume is reached. This distillation procedure is repeated twice. 4 ml of H_2O_2 and 10 ml of H_2O are then added and the solution boiled again. $KMnO_4$ solution followed by $FeSO_4$ are added until the solution is colorless. This solution is used for constructing the calibration curve, by adding to it known amounts of borate solution; it can also be used as the "solvent" by comparison with which the optical density can be determined both during construction of the calibration curve, and for determination of boron in steel samples of the same mark.

SUMMARY

1) It has been shown that it is possible to use carmine as a reagent for the spectrophotometric determination of boron in steel.

2) It has been found that addition of phosphoric acid to the solution of steel enables one to determine small amounts of boron both in carbon and in alloyed steels, without preliminary separation of heavy metals.

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DETERMINATION OF SILICON IN THE PRESENCE OF PHOSPHORUS, IRON, COPPER, MANGANESE, AND TITANIUM

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Determination of small amounts of silicon in the presence of phosphorus, arsenic, iron, and other accompanying elements is one of the most difficult problems in analytical chemistry. A very essential drawback of all colorimetric methods of determining silicon is the fact that phosphorus, arsenic, and germanium, just like silicon, form compounds of similar structure and color with ammonium molybdate. A number of methods have been suggested for removing phosphorus and iron so as to prevent interference on their part during colorimetric determination of silicon. All the same, removal of these elements leads to considerable loss of silicon. In view of this, methods have been suggested which permit determination of silicon in the presence of phosphorus and ron. The method of Nemets, Lanik, and Koppova [1] belongs to this category; their method is based on differences in the stability of the silicovanadomolybdic complex and the phosphorovanadomolybdic complex. The phosphorovanadomolybdic complex is less stable on standing, both in media of fairly high acidity (Kokorin [2]), nd in weakly alkali media (Nemets, Lanik, and Koppova), than the silicovanadomolybdic complex, thanks to which, the blue color from the phosphorus complex rapidly disappears, while the color of the silicon complex emains, and reaches its maximum intensity after one hour. These authors also point out that small amounts of ron do not interfere.

Our experiments showed [3] that colorimetric determination of silicon by means of the formation of the ilicovanadomolybdic complex, in the presence of phosphorus, iron, copper, manganese, and titanium does not ield reliable results.

EXPERIMENTAL

In order to study the formation of silico- and phosphorovanadomolybdic complexes, the light absorption solutions containing pyrophosphates, orthophosphates, and sodium silicate, both individually and when present nultaneously, was determined; similar determinations were made in the presence of copper, iron, manganese, d titanium.

Aqueous solutions of the salts indicated, taken in various proportions, were treated with 2.5 ml of 1% citric id and 2.5 ml of 5% ammonium molybdate. After 5 minutes, 3.4 ml of 4% sulfuric acid, 1 ml of 1% sodium nadate, and 1 ml of 5% sodium thiosulfate were respectively added to the solution. After 15 minutes the uid was made alkaline with 17.5 ml of a glycerol-sodium carbonate solution *, and the volume made up to ml with water; the light absorption of the colored liquid was determined at intervals over a period from 25 nutes to 6 hours after addition of reagents, using a horizontal Pulfrich photometer fitted with a S66 light er.

Our tests showed that pyrophosphates do not give colored reduction products under these conditions.

Silicates form reduction products, the intensity of whose color reaches a maximum after one hour and ains constant for some time.

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he glycerol-sodium carbonate solution was prepared by dissolving 6 g of anhydrous sodium carbonate in 60 of water and adding 10 ml glycerol.

When the solution contains 0.5 and 1.0 mg of phosphorus, it becomes completely colorless when kept at room temperature for 2 hours after addition of reagents. Nevertheless, solutions containing 2.0, 5.0, and 10 mg of phosphorus do not become colorless within this time. The color only disappears after 6-6.5 hours in this case (Fig. 1).

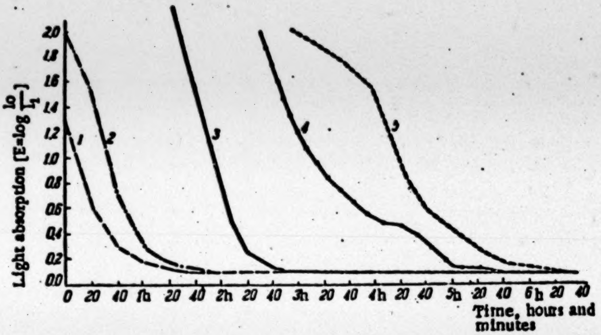

Fig. 1. Decrease in color intensity as a function of phosphorus concentration (without heating).
1) 0.5 mg P; 2) 1.0 mg ; 3) 2.0 mg P; 4) 10.0 mg P; 5) 5.0 mg P.

It was established that it is possible to reduce the time taken for the solution of phosphorovanadomolybdic complex to become colorless to 25-35 minutes, by heating the colored solutions on a water bath at a temperature not exceeding 50° (Fig. 2).

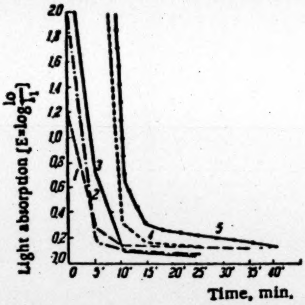

Fig. 2. Decrease in color intensity as a function of phosphorus concentration (on heating).
1) 0.5 mg P; 2) 1.0 mg P; 3) 2.0 mg P; 4) 5.0 mg P; 5) 10.0 mg P.

When the solution contained equal amounts of phosphorus and silicon (0.1 mg each), the color of the mixture corresponded to the color obtained when silicon alone was present in tests with pure solutions of sodium silicate. Addition of large amounts of phosphorus (0.5 and 1.0 mg) led to partial weakening of the color; the color which remains did not correspond to that obtained when silicon alone was used. Addition of 2.0 and 5.0 mg of phosphorus led to complete decolorization of the mixture – both complexes were broken down. Consequently, when the phosphorus content of the solution is not known, determination of silicon becomes impossible (Fig. 3).

In tests with mixtures containing phosphorus and iron (Fig. 4) it was found that iron (0.05-0.1 mg) does not affect decomposition of phosphorovanadomolybdate complex – the mixture was completely decolorized; 0.5 mg of iron prevented decomposition of the phosphorus complex to a considerable extent, and with increasing iron concentration (1.0, 2.0, 3.0, and 5.0 mg) the stability of the phosphorus complex increased – the mixture was not decolorized. Consequently when the solution contained 0.5 mg and more of iron, it was not possible to come to a reliable decision as to the amount of silicon present on the basis of the residual color.

During a study of the light absorption of mixtures containing phosphorus, copper, manganese, and titanium it was found that these cations affected decolorization of the phosphorovanadomolybdate complex, but to a considerably lesser extent than iron (Fig. 5).

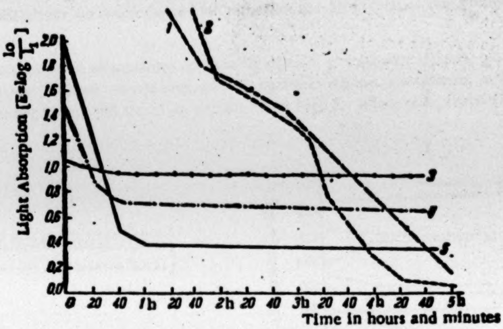

Fig. 3. Relation between light absorption and phosphorus concentration in the presence of 0.1 mg Si (in all cases).
1) 5.0 mg P; 2) 2.0 mg P; 3) 0.1 mg P; 4) 0.5 mg P; 5) 1.0 mg P.

When copper was present the color of the complex disappeared slower than when manganese and titanium were present; nevertheless, the color did not disappear altogether, so that in many instances incorrect results were obtained, because copper itself (in the absence of phosphorus and silicon) catalyzes formation of simple molybdenum blue, and the latter is completely decolorized when the medium is made alkaline.

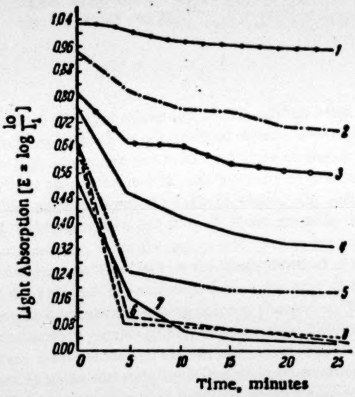

Fig. 4. Color intensity of the phosphorovanadomolybdic complex in the presence of various amounts of iron. In all cases 1.0 mg P was taken.
1) 5.0 mg Fe; 2) 3.0 mg Fe; 3) 2.0 mg Fe; 4) 1.0 mg Fe; 5) 0.5 mg Fe; 6) 0.1 mg Fe; 7) 0.1 mg Fe; 8) 0.05 mg Fe.

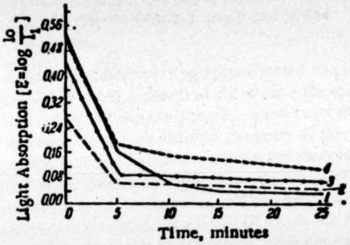

Fig. 5. Intensity of the color of the phosphovanadomolybdate complex in the presence of Cu, Mn, and Ti in amounts of 1.0 mg each; 1.0 mg of P was taken in each case.
1) P; 2) Ti and P; 3) Mn and P; 4) Cu and P.

During a study of the effect of iron, copper, manganese, and titanium on the stability of the silicovanadomolybdic complex (in the absence of phosphorus), it was shown that iron at a concentration of 0.1 mg in the test solution led to partial weakening of the complex color; copper, manganese, and titanium, at the concentrations we used, showed no effect on the formation of the silicovanadomolybdate complex (Fig. 6).

Changes in the light absorption of solutions containing silicon, phosphorus; silicon, phosphorus, and iron; silicon, phosphorus, and copper; silicon, phosphorus, and manganese; silicon, phosphorus, and titanium; silicon, phosphorus, iron, copper, manganese, and titanium are shown on Fig. 7. When phosphorus alone was present in solution, the light absorption of the solution after 25 minutes standing without heating approximated to zero. When the solution only contained silicon, and also when it contained equal amounts of silicon and phosphorus, the light absorption was 0.23. Addition of iron to mixtures containing silicon and phosphorus led to an increase in light absorption to 0.35; the intensity of the color of the mixture was greater than the intensity of the color of the complex formed by silicon alone. On adding copper to the mixture containing silicon and phosphorus, the light absorption fell to 0.13; titanium under the same conditions, caused the light absorption to drop to 0.09. Consequently, when the anions and cations mentioned are present, copper, manganese, and to a greater extent titanium show an effect on the break down of silicovanadomolybdate complex, as a result of which the intensity of the color which remains is less in the case of mixtures than when silicon alone is present. The light absorption of mixtures containing silicon, phosphorus, iron, copper, manganese, and titanium at the same time, is considerably greater (0.32), than the light absorption of a solution containing only silicon (0.24). Consequently, when these anions and cations are present simultaneously in the test solution, iron shows an essential effect, in that it favors the stability of the phosphorovanadomolybdate complex; nevertheless thanks to the presence of copper, manganese, and titanium which cause partial break down of the silicovanadomolybdate complex, the light absorption of this mixture is somewhat weaker (0.32) than the light absorption of a mixture containing silicon, phosphorus, and iron (0.35).

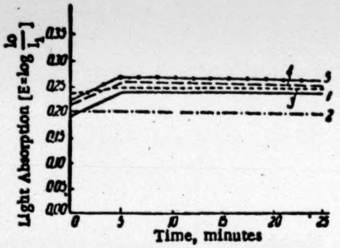

Fig. 6. Intensity of the color of the silicovanadomolybdate complex in the presence of Fe, Mn, Cu, and Ti in amounts of 1.0 mg each; 0.1 mg of Si was taken in each case.
1) Si; 2) Fe and Si; 3) Cu and Si; 4) Mn and Si; 5) Ti and Si.

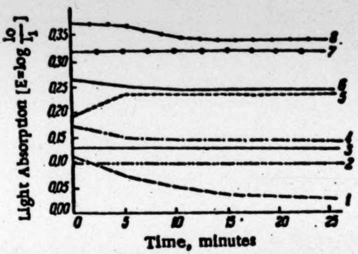

Fig. 7. Intensity of the color of the mixture of Si and P in presence of Fe, Cu, Mn, and Ti.
1) 1 mg P; 2) with 0.1 mg Si and P and 1.0 mg Ti; 3) with 0.1 mg P and S and 1.0 mg Mn; 4) with 0.1 mg Pu and Si and 1.0 mg Cu; 5) 0.1 mg Si; 6) with 0.1 mg P and Si; 7) with 0.1 mg P and Si and with 1.0 mg Fe, Cu, Mn, Ti; 8) with 0.1 mg P and Si and 1.0 mg Fe.

On the basis of results obtained during a study of the effect of iron, copper, manganese, and titanium on the break down of the phosphorovanadomolybdate complex and the stability of the silicovanadomolybdate complex, we concluded that determination of silicon in the presence of phosphorus, iron, copper, manganese, and titanium is not reliable.

SUMMARY

1) The possibility of determining silicon in the presence of phosphorus and other elements, as silico- and phosphorovanadomolybdate complexes has been studied.

2) In the presence of 0.5 mg and more of phosphorus in the test solution, determination of silicon becomes impossible as a result of complete decolorization of the solutions; break down of the phosphorovanadomolybdate complex leads to partial or complete break down of the silicovanadomolybdate complex as well.

3) Iron enhances the stability of the phosphorovanadomolybdate complex and favors the partial break down of the silicovanadomolybdate complex.

4) Titanium to a greater degree, and manganese and copper to a lesser extent, lead to breakdown of the silicovanadomolybdate complex in mixtures containing silicon and phosphorus.

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AMPEROMETRIC DETERMINATION OF SULFATE IONS

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Gravimetric determination of sulfate sulfur is one of the most difficult operations in analytical chemistry. Insufficient attention has been given to titrimetric determination of sulfate ions, and the methods which have been developed are only applicable in certain cases. With increasing use of amperometric methods, determination of soluble sulfates by titration with lead nitrate has become fairly widely used. Nevertheless, the high solubility of the latter even in comparatively dilute (< 0.1 N) solutions of other salts places a definite limit on the possibilities of the method. There are also published references [1] to the possibility of an amperometric determination of sulfate ions by back titration of excess $BaCl_2$ with chromate after precipitation of $BaSO_4$. In this case the method is based on amperometric determination of barium which has been studied fairly thoroughly [2]. Most authors recommend that barium should be titrated with chromate at 1.0-1.3 volt applied e.m.f. (against the saturated calomel electrode). Nevertheless, under these conditions, most heavy metals are reduced on the dropping mercury cathode, so that it is impossible to determine sulfate in the presence of such metals.

We made a study of the reduction of CrO_4^{2-} on a mercury cathode in relation to pH. pH was determined with a tube pH-meter using a glass electrode. Work was carried out with the aid of an automatic polarograph of the Geirovsky-Needla type; the mercury drops were artificially forced off the capillary tip.

Using a supporting electrolyte of 0.5-1.0 N ammonium acetate at a pH <6.5, a diffusion current can be observed for chromate at zero applied voltage. The polarograms obtained are shown on Fig. 1. The dotted line illustrates the relation between current strength at zero applied voltage and the pH of the solution. Nevertheless, as further experiments showed, under these conditions (pH about 6, applied e.m.f. = 0) direct proportionality between the value of the current and chromate concentration in solution is only maintained for chromate concentrations <0.0025 M. This is explained by the fact that at higher concentrations the diffusion current for chromate is obtained at more negative potentials. From the polarogram shown on Fig. 2 it is clear that at a potential of 0.2 volt, there is a direct proportionality between the value of the current and chromate concentration (straight line II) over a wide range of concentrations. Curve I (Fig. 2) illustrates the relation between current and chromate concentration at zero applied e.m.f. (saturated calomel electrode).

On the basis of the results obtained it can be concluded that the optimum conditions for amperometric titration of barium with chromate are a pH of <6.5; e.m.f = 0.2 volt (saturated calomel electrode). Nevertheless, the fact that there is a direct relation between current strength and chromate concentration up to concentrations of the latter of 0.0025 M, indicates that it should be possible to carry out an amperometric determination of barium at zero applied e.m.f. Under these conditions ions of most metals, as well as oxygen, are not reduced on the mercury cathode.

The pH limits within which reduction of chromate occurs even at zero applied e.m.f. (Fig. 1) ensure quantitative precipitation of barium as $BaCrO_4$. As Vasilyev and Popel [2] have shown, satisfactory results for determination of barium can be obtained at pH 4-7. According to our results, the pH limits are restricted to much narrower limits, namely 5.0-6.5, the optimum pH value being between 5.6 and 6.3 (Fig. 3). Warshowsky and coworkers [1] came to the same conclusion. At pH<5, near the equivalence point, there is observed a significant increase in current strength; the point does not lie on the straight line and the result obtained is considerably lower than theoretical; it is the result of the increase in solubility of $BaCrO_4$. Alcohol does not show an appreciable effect on the experimental results, but the presence of 15-20% of C_2H_5OH favors rapid attainment of a constant value of the current during titration.

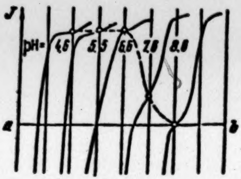

Fig. 1. Effect of the pH of the medium on reduction of CrO_4^{2-}. Polarograms were taken anodically-cathodically in a supporting electrolyte of 1 N CH_3COONH_4; S = 1:100; $C_{CrO_4^{2-}}$ = 1.2 × 10^{-3} M. The zero abscissa on each curve is marked by a point; ab – the zero line of the galvanometer.

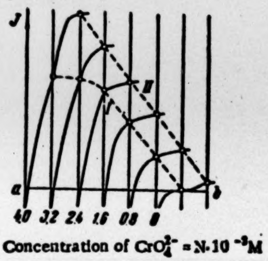

Fig. 2. Relation between current strength and CrO_4^{2-} concentration in solution at zero applied e.m.f (Curve I), and at 0.2 volt (Straight line II) (saturated calomel electrode). Polarograms were taken anodically-cathodically in a supporting electrolyte of 1 N CH_3COONH_4; pH 6.2; S = 1:150; ab – zero line of the galvanometer.

According to Warshowsky [1], during amperometric determination of barium in the presence of other salts, the results obtained are appreciably lower than theory. The same author also indicates that it is impossible to use buffer solutions for regulating the pH as a result of strong inhibition of formation of $BaCrO_4$ precipitate. All the same, the results of Vasilev and Popel [2], as well as our own results, do not confirm Warshowsky's conclusions. Other salts ($ZnCl_2$, $CdCl_2$, $NiCl_2$, NaCl, NH_4Cl) in concentrations up to 0.5-1.0 N have only a small effect on the experimental results (relative error ≤1%). The rate of formation of $BaCrO_4$ precipitate in buffered media (0.1-1.0 N CH_3COONH_4) is high enough in the presence of alcohol.

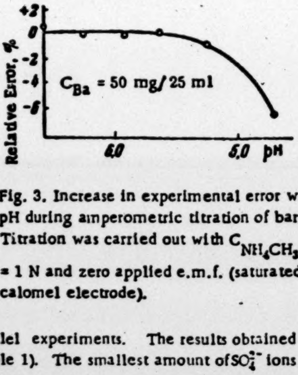

Fig. 3. Increase in experimental error with pH during amperometric titration of barium. Titration was carried out with $C_{NH_4CH_3COO}$ = 1 N and zero applied e.m.f. (saturated calomel electrode).

On the basis of the experimental results obtained, we have developed a technique for determining sulfate ions in the presence of appreciable amounts of alkali salts and the salts of some of the heavy metals.

A determination was carried out by adding a known volume of standard (about 0.07 N) solution of $BaCl_2$ to 25 ml of test solution which had been acidified with 1 ml of HCl (1:1) and heated to boiling. After precipitation of $BaSO_4$, the solution was cooled, and neutralized using Methyl Orange as indicator; 5 ml of 5 N CH_3COONH_4 solution was added, the pH then became 5.5-6.2. Excess barium chloride was titrated amperometrically with K_2CrO_4 solution (0.07 M) at an applied e.m.f. of zero. Test solution contained 0.2-0.5 N zinc salts, and sodium chloride at a concentration of 0.5-1.0 N.

Sulfate ions were determined gravimetrically in parallel experiments. The results obtained by both methods were in satisfactory agreement with each other (Table 1). The smallest amount of SO_4^{2-} ions which could be determined with sufficient accuracy amounted to 3-4 mg.

To method developed was used for determining lead sulfate in the active mass of lead accumulators and for determination of sulfate in nickel hydroxide.

TABLE 1

Determination of Sulfate Ion in Solutions Containing Zinc

Exp. No.	Found, in mg		Error	
	Gravimetrically	Amperometrically	in mg	in %
1	227.5	228.2	+0.7	+0.3
2	197.6	196.8	—0.8	—0.4
3	131.0	130.5	—0.5	—0.4
4	75.5	75.7	+0.2	+0.3
5	53.3	53.8	+0.5	+0.9
6	32.6	32.9	+0.3	+1.0

The mass of positively charged plates was treated with hydrochloric acid for converting PbO_2 into $PbCl_2$, after which the lead was precipitated from acid solution by means of zinc shavings. Reduction of lead with zinc during analysis of the mass of negatively charged plates was carried out in an acetate mixture consisting of equal volumes of 5N CH_3COOH and 5N CH_3COONH_4. Sulfate ions were determined in the solutions obtained by the method described above. During analysis of nickel hydroxide the latter was dissolved in the minimum amount of HCl, after which sulfate was titrated amperometrically.

The accuracy and reproducibility of the results obtained depended essentially on the ratio of the volume of $BaCl_2$ used for precipitating SO_4^{2-} and the volume back titrated with potassium chromate. The most accurate results were obtained when a small excess of $BaCl_2$ was used for precipitating SO_4^{2-}. Nevertheless, visual indication of completeness of precipitation of $BaSO_4$ and the appearance of excess $BaCl_2$ in solution is difficult. Accordingly, during analysis of samples with widely varying sulfate contents, it is necessary to carry out a preliminary rough titration for establishing the volume of $BaCl_2$ required for precipitating sulfate. This complicates and slows down analysis.

In order to overcome these disadvantages we should like to propose an express method based on "double titration"; this consists essentially of the following:

Test solution after neutralization and addition of ammonium acetate was titrated amperometrically at zero applied e.m.f. with standard barium chloride. 3-5 ml lots of the latter were added immediately. Completion of sulfate precipitation was indicated by chromate ions, a standard solution of which (K_2CrO_4) was added in small portions (3-5 drops) from a buret after addition of each new portion of barium chloride. When sulfate precipitation was not complete (absence of Ba^{2+} in solution), introduction of CrO_4^{2-} into the solution led to a sharp increase in current strength. When sulfate ion precipitation was complete and excess $BaCl_2$ was present in solution, the latter was complexed as $BaCrO_4$ and the galvanometer needle remained in its original position.

When precipitation of SO_4^{2-} was complete, 5 ml of alcohol was added to the solution, and excess $BaCl_2$ titrated with potassium chromate from the same buret. When such a method was used, independently of the

TABLE 2

Determination of Lead Sulfate in the Active Mass of Lead Accumulators

Sample number	Hot acid solution			Cold neutral solution			
	Gravimetric method	Amperometric method		Amperometric method		Amperometric method with coprecipitation correction factor	
	$PbSO_4$ found, %	$PbSO_4$ found, %	Error, in %	$PbSO_4$ found, %	Error, in %	$PbSO_4$ found, %	Error, in %
1	2.57	2.48	—3.5	2.60	+1.2	2.60	+1.2
2	7.38	7.43	+0.7	7.34	—0.5	7.34	—0.5
3	9.13	9.21	+0.9	9.22	+1.0	9.22	+1.0
4	16.4	16.6	+1.2	15.8	—3.6	16.3	—0.6
5	21.8	22.0	+0.9	21.3	—2.3	22.0	+0.9
6	39.6	40.0	+1.0	38.4	—3.0	39.6	0
7	39.9	40.4	+1.3	38.9	—2.5	40.1	+0.5
8	59.4	60.0	+1.0	57.5	—3.2	59.3	—0.2

amount of sulfate being determined, the excess of standard $BaCl_2$ did not exceed 3-5 ml in all cases; this ensured reasonable reproducibility of the results.

Nevertheless, when working with this "double titration" method it is necessary to precipitate barium sulfate in neutral, cold, solutions, and this unavoidably leads to appreciable errors as the result of coprecipitation of the sulfates of alkali and heavy metals. It is clear from Table 2, that by carrying out a preliminary precipitation of SO_4^{2-} from a hot, acid solution, the technique described is capable of giving satisfactory results independently of the absolute amounts of lead sulfate in the test material. The error does not exceed 1-1.5% relative in most cases.

When the "double titration" method (precipitation of $BaSO_4$ from cold neutral solutions) was used on samples with lead sulfate contents greater than 10%, the results obtained were significantly low (Table 2). This is caused presumably by adsorption of the sulfates of alkali and heavy metals when large amounts of $BaSO_4$ are precipitated. To a first approximation it can be assumed that the amount of coprecipitated soluble sulfates is proportional to the amount of $BaSO_4$ precipitate; on this assumption the relative error of determination of SO_4^{2-} ions at concentrations of the latter greater than 25 mg/25 ml, remains practically constant and equal to about 3% relative. The introduction of an empirical correction factor of 1.03 for the effect of coprecipitation leads to satisfactory results for any concentration of lead sulfate in the mass of the accumulator plates.

TABLE 3

Determination of Sulfates in Production Samples

No. of test sample	Positive active mass of lead accumulator			Negative active mass of lead accumulator			Nickel hydroxide			Cadmium electrolyte		
	$PbSO_4$ found, in %			$PbSO_4$ found, in %			SO_4^{2-} found, in %			SO_4^{2-} found, in g/liter		
	Gravimetric	Amperometric	Error, in %	Gravimetric	Amperometric	Error in %	Gravimetric	Amperometric	Error in %	Gravimetric	Amperometric	Error in %
1	2.20	2.15	—2.3	16.3	16.3	0	8.60	8.40	—2.3	110.2	109.0	—1.1
2	4.20	4.28	+1.9	24.5	24.8	+1.2	0.60	0.58	—3.3	126.5	127.2	+0.6
3	6.71	6.74	+0.4	40.3	40.1	—0.5	0.56	0.55	—1.8	131.0	132.5	+1.1
4	11.6	11.4	—1.7	53.9	53.6	—0.6	4.50	4.40	—2.2			
5	21,3	21.1	—0.9	63.0	62.4	—0.9						
6	52.6	52.2	—0.8									

The suggested "double titration" method gives reasonably reproducible results; the accuracy is satisfactory for express methods of analysis. A determination does not take more than 10 minutes. Results for determinations of lead sulfate in the active mass of lead accumulators, and for sulfate in nickel hydroxide and in cadmium electrolytes are given in Table 3.

SUMMARY

1) A method has been worked out for amperometric determination of barium in the presence of heavy metals* and atmospheric oxygen.

2) A method has been developed for determination of sulfate ion in the presence of large amounts of alkali and heavy metals*; it is based on precipitation of sulfate ions as $BaSO_4$ and amperometric determination of excess $BaCl_2$ by titration with potassium chromate at zero applied e.m.f.

3) On the basis of the work carried out, an express method is suggested for determination of soluble sulfates. The method has been verified on production samples and has been adopted in the laboratory of the Scientific Research Accumulator Institute.

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* Apart from metals reduced at potentials which are more positive than 0.2 volt applied e.m.f. (saturated calomel electrode).

DETECTION OF SELENIUM BY MEANS OF PHENYLANTHRANILIC ACID

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Various organic reagents are in use for detecting selenium [1, 2, 5-9, 11-13]. Nevertheless, methods of detecting and determining selenate and selenite ions by means of organic reagents which change their color on oxidation have not yet been widely used.

By selecting indicators with differing values of the oxidation-reduction potential and eliminating the effect of interfering elements, there is a possibility of developing methods of detecting selenium both in solutions of its pure salts as well as in the presence of other elements.

Of the various oxidation-reduction indicators we chose N-phenyl anthranilic acid (o-diphenylaminecarboxylic acid). This acid was first suggested as an oxidation-reduction indicator by Syrokomsky and Stepin [3]. Phenylanthranilic acid is one of the most stable oxidation-reduction indicators and has a fairly high oxidation-reduction potential.

Both selenate SeO_4^{2-} and selenite SeO_3^{2-} ions can react with phenylanthranilic acid. The normal oxidation-reduction potential of the system SeO_4^{2-}/SeO_3^{2-} is equal to 1.08 volt [4]. For the system SeO_3^{2-}/Se, the value is 0.74 volt. Oxidation-reduction potentials of the given systems increase appreciably on increasing the acid concentration, since the reduction reactions of selenate to selenite ion, and of selenite ion to elemental selenium occur with participation of hydrogen ions:

$$SeO_4^{2-} + 2H^+ + 2e \rightleftarrows SeO_3^{2-} + H_2O.$$
$$SeO_3^{2-} + 6H^+ + 4e \rightleftarrows Se + 3H_2O.$$

The normal oxidation-reduction potential of the system $Fak_{ox.}/Fak_{red.}$ * is 1.08 volt. In neutral or weak acid solution, selenate and selenite ions do not oxidize phenylanthranilic acid, but when the sulfuric acid concentration is increased considerably (up to 24 N), the potential of the systems SeO_4^{2-}/SeO_3^{2-} and SeO_3^{2-}/Se increase to such an extent that selenate and selenite ions can oxidize phenylanthranilic acid.

On increasing sulfuric acid concentration of the solution, the oxidation-reduction potential of the system should decrease, since the equilibrium of the reaction:

$$2\ Fak_{red} \rightleftarrows Fak_{ox} + 4\ H^+ + 4\ e,$$

should be displaced from right to left on increasing the hydrogen ion concentration.

The concentration of sulfuric acid in solution and the amount of phenylanthranilic acid are of great importance for detection of selenate and selenite ions by means of phenylanthranilic acid.

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* $Fak_{ox.}$ is the oxidized form of phenylanthranilic acid; $Fak_{red.}$ is the reduced form of phenylanthranilic acid.

1. Study of the Reaction Between Selenate Ions and Phenylanthranilic Acid

When selenate ions are allowed to react with phenylanthranilic acid in a strong sulfuric acid solution under the action of heat, a cherry or blue-violet color is formed. Pure sulfuric acid does not react with phenylanthranilic acid either when cold or on heating. No color is observed in hydrochloric acid solution either. The cherry color is not stable; the solution becomes colorless rapidly and a flocculent precipitate separates out. The blue-violet color is considerably more stable and may persist for several days. This color is only formed when the sulfuric acid concentration of the solution is high enough.

Optimum conditions for formation of the blue-violet color are created by using sulfuric acid concentrations greater than 24 N. At such concentrations the blue-violet color appears rapidly and exhibits its highest intensity and stability.

The color exhibits its highest intensity in solutions containing 0.0003-0.0006 g of phenylanthranilic acid. For greater amounts of phenylanthranilic acid the color weakens, while at very high concentrations no color appears at all. In the latter instance a precipitate of elemental selenium separates out. Presumably as a result of the presence of a large excess of phenylanthranilic acid, the latter is only oxidized to colorless diphenylbenzidenedicarboxylic acid.

The sensitivity of the reaction between selenate ions and phenylanthranilic acid was determined by introducing 3 ml lots of 24 N sulfuric acid into a series of test tubes. 0.03 ml of 1% phenylanthranilic acid solution and 0.03 ml of selenious acid of various concentrations (10^{-2} - 10^{-8} g/ml) was then added to each test tube. Test tubes plus their contents were heated to 70-80°. Observation of the development of a blue-violet color was observed. The limiting sensitivity of the reaction of the selenate ion with phenylanthranilic acid was found to be 5×10^{-7} g of selenium/ml.

As pointed out already, on adding a small amount of phenylanthranilic acid solution to 24 N sulfuric acid containing selenious acid, a blue-violet color is observed. This coloration indicates that phenylanthranilic acid is oxidized by selenate ions to the violet diphenylbenzidenedicarboxylic acid. On adding to the same solution a large excess of phenylanthranilic acid no color is observed and a precipitate of elemental selenium is formed. It may be assumed in this case that phenylanthranilic acid is only oxidized to the colorless diphenylbenzidenedicarboxylic acid. As for the selenate ion, it might be thought that under the action of small amounts of phenylanthranilic acid it is only reduced to the selenite ion. This assumption, however, is not confirmed by experiment. When the blue colored solution is strongly diluted with water, its color changes first to cherry and then the solution becomes colorless. Under these conditions elemental selenium, which can be readily removed by flotation with isoamyl alcohol, separates out from solution in addition to the phenylanthranilic acid. Apparently, in all cases the selenate ion is reduced to elemental selenium, but, depending on its concentration in solution, phenylanthranilic acid can be oxidized either to colorless diphenylbenzidenedicarboxylic acid or to the violet diphenylbenzidenedicarboxylic acid.

2. Study of the Reaction Between Selenite Ions and Phenylanthranilic Acid

The optimum sulfuric acid concentration for reaction between selenite ions and phenylanthranilic acid is 24 N, though the theoretical value of the oxidation-reduction potential of the system SeO_3^{2-}/Se, for such a normality, does not exceed the value of the potential of the system $Fak_{ox.}/Fak_{red}$.

This reaction requires almost the same amount of phenylanthranilic acid, i. e. 0.03-0.06 ml of a 1% solution of phenylanthranilic acid for 3 ml of 24 N sulfuric acid containing 10^{-2}-10^{-8} g selenium as sodium selenite. On addition of a very large amount of phenylanthranilic acid no color appears and a precipitate of elemental selenium separates out.

The sensitivity of the reaction between selenite ions and phenylanthranilic acid is somewhat less than the corresponding one with selenate ions. The limiting sensitivity was found to be about 10^{-6}g in 1 ml.

Since, on adding a large excess of phenylanthranilic acid to a sulfuric acid solution of selenite ions no blue color is observed and a precipitate of elemental selenium is formed, while on dilution with water of a blue-violet colored solution decolorization occurs (just as with selenate ions) and selenium is again precipitated in the elemental state, the following conclusions can be drawn regarding the chemistry of the reactions.

On addition of small amounts of phenylanthranilic acid it is oxidized by selenite ions to the violet diphenylbenzidenedicarboxylic acid. When a large excess of phenylanthranilic acid is used, it is oxidized only to colorless diphenylbenzidenedicarboxylic acid. As for selenium, it is reduced (like the selenate ion) in both cases to the elemental state; in the first instance however it separates out in a finely dispersed state to form a colloidal state, while in the second case selenium separates out in a coarsely dispersed state.

A Method of Detecting Selenium

a) Detection of Comparatively Large Amounts of Selenium (Test solution contains not less than 5.0 mg selenium/ml as SeO_3^{2-} or SeO_4^{2-}). Into a micro test tube (or an ordinary test tube) of heat resistant glass is introduced 1 ml of a mixture of two volumes of concentrated, chemically pure sulfuric acid, free from oxidizing and reducing agents, and one volume of twice distilled water, or 24 N sulfuric acid solution prepared beforehand. 1 drop (approximately 0.03 ml) of a 1% solution of phenylanthranilic acid in concentrated sulfuric acid and 1 drop of test solution are then added. When selenium is present, a blue-violet color develops, the intensity of which depends on the selenium content of test solution.

b) Detection of Small Amounts of Selenium (Test solution contains less than 5 mg selenium/ml). In a micro test tube (or ordinary test tube) is mixed 0.5 ml of test solution with 1 ml of concentrated sulfuric acid. One drop of a 1% solution of phenylanthranilic acid is added and the mixture heated almost to boiling. A blue-violet color appears when selenium is present.

Using this method it is possible to detect 5×10^{-7} g of selenium as SeO_4^{2-} at a dilution of 1:100,000 or 3×10^{-6} g of selenium as SeO_3^{2-}.

A spot technique can also be used. One drop of test solution is placed on a watch glass followed by 1 drop of concentrated sulfuric acid and 1 drop of a 0.1% phenylanthranilic acid solution in concentrated sulfuric acid. The whole is mixed and carefully heated. A blue color is observed when selenium is present.

Using this spot technique it is possible to detect 10^{-7} g of selenium in a drop of test solution (0.03 ml) as SeO_4^{2-} and 10^{-6} g of selenium as SeO_3^{2-}.

Trivalent antimony and arsenic, quadrivalent tin, molybdenum, copper, aluminum, zinc and thallium do not interfere with selenium detection. The following interfere with the selenate ion: divalent tin and iron, trivalent iron, as well as oxidizing agents and reducing agents.

It is possible to use the reaction of phenylanthranilic acid with selenate and selenite ions respectively for photometric determination of selenium, since the colored solutions obey Beer's law (Table).

Concentration		Ratio of concentration of standard solution to test solution	Height		Ratio of heights of standard solution to test solution
Standard selenium solution, in mg/ml	Test selenium solution, in mg/ml		of standard solution	of test solution	
0.40	0.32	1.25	1.2	1.5	1.25
0.40	0.32	1.25	1.6	2.0	1.25
0.20	0.16	1.25	1.82	2.25	1.25
0.20	0.16	1.25	2.41	3.0	1.245
0.10	0.16	0.625	6.35	4.00	0.63

The blue-violet solutions were diluted with 24 N sulfuric acid and were measured on a Duboscq colorimeter.

SUMMARY

A technique has been developed for detecting selenate and selenite ions by means of phenylanthranilic acid.

Optimum conditions have been established for carrying out the reactions between selenate and selenite ions respectively with phenylanthranilic acid.

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MICRO DETERMINATION OF ELEMENTAL FLUORINE

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Available literature on the analytical chemistry of fluorine does not touch upon determination of elemental fluorine [1]. Our problem was to develop a method for determining elemental fluorine in air. In trying to solve the problem confronting us we could not resort to use of conversion of F_2 into the fluoride ion, since HF almost always accompanies elemental fluorine. The strong oxidizing properties of fluorine seemed to offer good possibilities for developing a method.

The gaseous fluorine required for tests was diluted with nitrogen to give a concentration of 4.3% by weight. The gaseous mixture was contained in an iron cylinder under a pressure of 10 atmospheres. For preparing gaseous mixtures containing lower F_2 concentrations, small amounts of the stock mixture were transferred by means of small gas pipets to 8-10 liter bottles with ground glass necks assembled like Drechsel flasks. Gas pipets and the flasks used for the diluted mixtures were dried with dry air beforehand. Ground glass joints and taps were lubricated with a special grease; polychlorinated rubber was used for connections. Gas was transferred from the pipet by creating a vacuum in the vessel used for containing the final mixture, and then allowing dry air into the flask to destroy the remaining vacuum. The gaseous-air mixture was kept in the flask for 3 hours after the taps had been closed; fluorine concentration was then established iodometrically.

Collection of test air by drawing it through various types of absorbing media was carried out while the inlet tap of the bottle was kept closed in order to avoid decreasing the fluorine concentration. By doing this up to 0.5 liter of air could be collected; the vacuum had to be destroyed at this stage; the air used for this purpose was dried by passing it through a flask containing concentrated H_2SO_4.

The reagents listed in Table 1 proved to be the most suitable for detecting and determining traces of fluorine in air.

TABLE 1

Reaction for Elemental Fluorine

Reagent	Results of reaction
o-Tolidine, solution in HCl	Yellow color
Dimethylparaphenylenediamine (Alftan's reagent)	Red color
Phenetidine, acetic acid solution	Violet color
Methyl Orange, acidified solution	Decolorization-weakening of the color
Fuchsin, acidified solution	Decolorization-weakening of the color
Aniline + phenol + alkali	Blue color (indophenol reaction)
Luminol, dilute alkali solution	Extinction of fluorescence (highly sensitive reaction)
Fluorescein on silica gel	Red color (formation of eosin)
KI solution + starch	Blue color
Fe^{2+} + NH_4SCN, acidified solution [13]	Red color

Thus, elemental fluorine gives a series of color reactions which are characteristic of highly active oxidizing agents. Fluorine reacts with o-tolidene [2-4], with fluorescein, with dimethylparaphenylenediamine [5, 6], and weakens the intensity of the color of Methyl Orange [7, 8], Methyl Red, fuchsin [9] and others. The similarity between chlorine and fluorine from an analytical point of view was particularly clearly expressed. Fluorine, like chlorine, also gives the indophenol reaction, despite what Kulberg and Borzova state [10, 11] regarding the specificity of this reaction for free chlorine.

An Express Method for Determining Elemental Fluorine

The method is based on liberation of free bromine from potassium bromide by means of fluorine, and subsequent interaction of the bromine with fluorescein to form tetrabromofluorescein (eosin) which has a red color.

TABLE 2

Establishment of the Proportionality Coefficient of the Color Line (mm) and the Amount of Fluorine (γ)

Amount of F_2, in γ	Length of colored zone in mm	Proportionality coefficient (γ F_2 per mm)
15.0	38	0.40
10.0	33	0.30
7.5	25	0.30
5.5	16	0.34
5.5	16	0.34
5.0	16	0.31
5.0	14	0.35
4.5	12	0.37
3.6	11	0.32
3.2	9	0.35
2.5	7	0.35
2.4	8	0.30
2.25	7	0.32
2.0	6	0.33
2.0	6	0.33
1.5	4	0.37
		0.336

On drawing air through an indicator tube filled with silica gel soaked with a solution of fluorescein, the original yellow color of the filler changed to red. Other conditions being equal the length of the red colored zone in the indicator tube was proportional to the amount of fluorine. The zone length (in mm) was then used for calculating the amount of fluorine, using the coefficient determined experimentally beforehand. Under the conditions which we used, 1 mm of colored zone was proportional to 0.34 γ fluorine (Table 2).

It must be emphasized that it is essential to ensure that the indicator tubes are prepared under strictly standard conditions and that the air be drawn through at a constant rate.

Indicator tubes were prepared in accordance with Kozlyaeva and Vorokhobin's technique [12].

Coarse silica gel which had been ground was passed through a 260-300 μ sieve. This fraction of silica gel was treated twice with 6 N HCl by boiling with the latter, it was then washed with water until no reaction was obtained for chloride ions; it was finally dried and calcined at 750°. The solution of fluorescein used for soaking the silica gel was prepared as follows: 30 g of KBr + 1 g of K_2CO_3 were dissolved in 100 ml of water and 0.1 g fluorescein added, the latter having being dissolved beforehand in 1 ml of 10% KOH. Before use, part of this solution was taken and diluted with distilled water in the proportion 1:5. An aliquot of the sieved silica gel was treated with the dilute fluorescein solution using 1.2 ml of solution per g of silica gel; silica gel and solution were thoroughly mixed and then dried in an oven. This powder was used for filling glass tubes 90 mm long and 2.5 mm in diameter; a wad of cotton wool was fitted at one end of the tube and the powder strewn in through the other using a funnel with a drawn out stem for this purpose. By closing the top end with the finger and gently tapping the tube on the wall, the column of powder was packed down; the length of the final column of powder was 75 mm. Another wad of cotton wool was then pressed down onto the free surface of the silica gel powder by means of a thin metal rod. Both ends were finally plugged and the tube stored rolled up in black paper.

Fluorine in air was determined as follows: the plugs were removed from one of the indicator tubes, and one end connected to a small aspirator (1-2 liters); air was drawn through at a steady rate until 1 liter had been collected in the course of 20 minutes. Instead of an aspirator, it is possible to use an air sampling system of the type supplied by the All Union Scientific Research Institute of Occupational Hygiene and Diseases in Leningrad. The length of the red colored zone (if any) was measured with a millimeter scale and elemental fluorine concentration of test air calculated.

The method has a sensitivity of 0.34 γ of fluorine / liter when 1 liter of air is used for analysis.

A Colorimetric Method for Determining Elemental Fluorine

In this method use was made of the capacity of elemental fluorine to decolorize colored solutions of Methyl Red. When air is drawn through a highly dilute, acidified solution of Methyl Red, the original color of the latter weakens to an extent which is proportional to the amount of fluorine; the reaction is speeded up appreciably in the presence of potassium bromide.

The intensity of the residual color was measured by comparison with a series of standards; the latter can be prepared from Chloramine T containing known amounts of active chlorine. A special series of tests carried out with the object of comparing the effect of fluorine and chlorine (the latter as Chloramine T) on solutions of Methyl Red demonstrated that equal amounts of these materials weaken the color of such solutions to approximately the same extent.

Absorbent Solution. 0.005 g of Methyl Red was dissolved in 20 ml alcohol, 50 ml of 5% sulfuric acid and 0.5 g of KBr were added, and the volume made up to 1 liter with water.

Standard Scale. A solution of Chloramine T equivalent to 3.5 γ of free chlorine / ml was used for preparing the standards; the solution was standardized iodometrically. 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, and 0.12 ml of standard solution was introduced into a series of colorimeter tubes; these amounts of solution corresponded to 0, 0.35, 0.70, 1.4, 2.1, 2.8, 3.5, and 4.2 γ of chlorine. The volume in each tube was made up to 0.12 ml and 2 ml of absorbent solution added to each with thorough agitation. Elemental fluorine was then determined by means of the following simple operations: air to be tested was drawn through two micro absorbers connected in series at the rate of 10 liter/hour; the absorbers which were of the Polezhaev type contained 2 ml of absorbent solution; the intensity of the residual color was then compared with the colors of the standards. The method has a sensitivity of 0.35 γ F_2 in a volume of 2 ml.

SUMMARY

Quantitative methods of determining traces of elemental fluorine in air have been developed which are based on the reactions of F_2 with fluorescein and Methyl Red respectively.

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METHODS FOR THE ISOTOPIC ANALYSIS OF WATER

5. FLOTATION METHOD WITH AN ACCURACY OF ± 0.2 γ

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The method described below is designed for isotopic analysis of natural waters. It ensures reliable measurement of differences in the density of water to an accuracy of ± 0.2 γ/ml. This accuracy is achieved by using an improved method of purifying the water, by filling the measuring apparatus with the purified water without leaving access to air, by increasing the sensitivity of the float, by using a thermostat operating at an accuracy of ± 0.0005°, and by introducing a series of corrections.

Purification of the Water

The first stage in purifying water (100 ml) is carried out in an apparatus made from stable glass, and consists of the following operations: 1) oxidation of impurities in an alkaline medium (0.3 g $KMnO_4$ and 0.1 g NaOH); 2) distillation, during which the flask containing the water is connected through a crossover system as shown in Fig. 1; 3) oxidation in an acid medium (0.1 g of $KMnO_4$ and 2 drops of H_2SO_4); 4) distillation; 5) distillation.

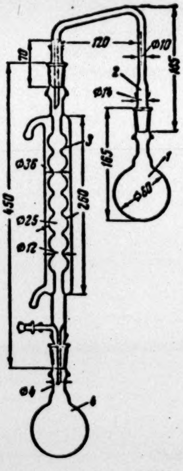

Fig. 1. Apparatus for oxidizing impurities and distilling the water. 1) flask for test samples; 2) crossover system; 3) spherical condenser; 4) receiver.

During oxidation, the side tube of the condenser is closed with a cap. The last two distillations are carried out in clean apparatus. During each distillation, 5% of the water is distilled off into a graduated cylinder, and the same amount left in the flask.

For complete removal of volatile impurities it is recommended that distillation be carried out in a stream of nitrogen [1]. The latter is passed into the apparatus used for purification from a cylinder at the rate of 300 cm^3/minute; it is passed through a packed glass filter and trap cooled in liquid air (Fig. 2b). Distillation is carried out in a glass apparatus (Fig. 2a) except that a flask is connected instead of the special receiver and measuring apparatus described below. During distillation the setup is connected to the apparatus via tap 4 and a bubble counter. In order to wash the condenser an individual portion of water (5 ml) from the fifth operation is first of all distilled completely. The residual water is then distilled in a quartz flask, the first and last fractions (5% each) being discarded. The amount of distilled water and discarded fractions is controlled by weighing the flasks closed with ground glass stoppers.

The last distillation is carried out like the previous one, except that all the apparatus used is made from quartz, and that to the lower ground joint of the condenser is connected (as shown in Fig. 2a) a special quartz receiver shown in Fig. 3. A siphon ending in a ground joint is fused into the receiver; this joint is connected to the measuring apparatus (Fig. 4) made of Jena glass. The latter consists of a test tube with a float 2 (the float is of the form described in [2]). The quartz float and the way it is prepared are shown separately in Fig. 5

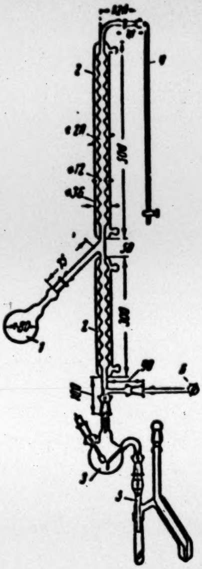

Fig. 2a. Apparatus for distilling water in a stream of nitrogen.
1) flask for sample; 2) spherical condenser; 3) receiver + electrodes; 4) outlet tube + tap; 5) apparatus for float measurement; 6) three way tap.

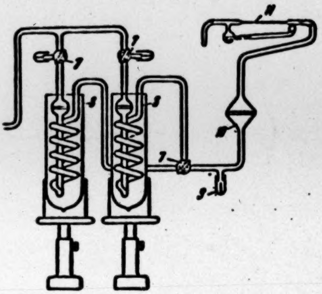
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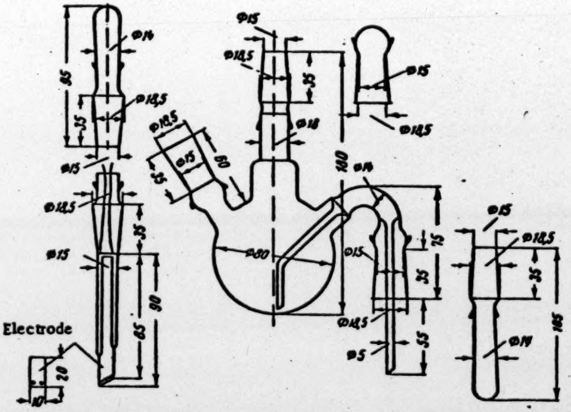
Fig. 2b. Setup for nitrogen purification
7) three way tap; 8) trap; 9) valve; 10) glass filter; 11) rheometer.


Φ14
Φ18,5
85
35
Φ15
Φ18,5
35
Φ15
90
65
Electrode
20
10
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Φ18
35
160
Φ18,5
Φ15
60
35
Φ14
Φ80
Φ15
75
35
Φ18,5
Φ5
55
Φ15
Φ15
Φ18,5
Φ18,5
35
165
Φ14

Fig. 3. Receiver.

as well as vessel 3 which is usually closed by means of cap 10. When the latter has been removed, nitrogen is passed through the system in order to expel the air, and 40 ml of the twice distilled water is introduced into vessel 3 while the nitrogen is flowing; the apparatus is sealed with cap 10 and all the water distilled in the nitrogen stream into the receiver; the specific electrical conductivity of the water is then measured (normally it is equal to 7-8 × 10^{-7} ohm^{-1} cm^{-1}).

When the measuring apparatus has already been used and there is a water lock in it, then, using ground glass joint 7, it is connected to the condenser; caps 5 and 6 are removed in a stream of nitrogen, the apparatus is opened and the receiver connected. The ground joints in the latter are opened and the air expelled with nitrogen. The receiver is then stoppered while nitrogen is still flowing, and then having removed the apparatus from the condenser, the former is turned round so that the neck of the receiver can be fitted on conveniently; when this has been done nitrogen is passed for a further period. The ground glass joint 7 of the apparatus is stoppered with the cap 10, electrodes are fitted into the receiver and the water distilled into the receiver; the apparatus is then filled as described above.

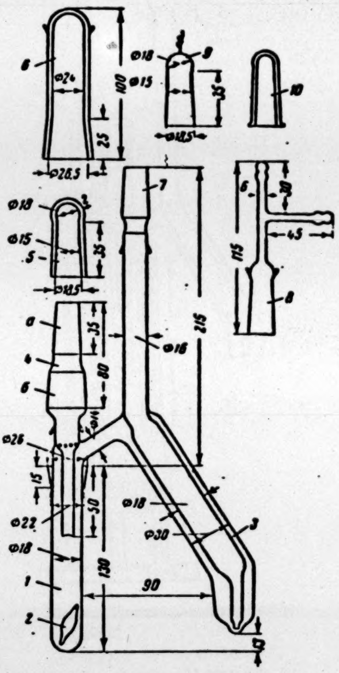

Fig. 4. Apparatus for making measurements on the float.
1) test tube + water; 2) float; 3) vessel + seal; 4) ground glass joint; 5) cap; 6) cap; 7) ground glass joint; 8) cap; 9) cap with spiral; 10) cap.

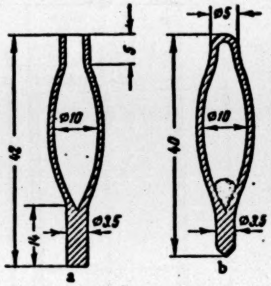

Fig. 5. Preparation of the float and finished float.

Filling the Measuring Apparatus With Purified Water

The receiver is kept for some time in a bath kept at a temperature 2-3° higher than that in the thermostat in which the equilibrium flotation temperature of the float is to be measured.

Having closed tap 4 (Fig. 2a) and removed the cap from the apparatus (Fig. 4), water is transferred under nitrogen pressure into the apparatus for measurement. The water which remains in the receiver acts as a seal to prevent air from getting into the measuring apparatus. When the electrodes have been removed from the receiver, the latter, together with the apparatus used for measuring, are disconnected from the condenser and reconnected to it by means of ground glass joint 7 of the apparatus. The receiver is disconnected from the apparatus in a nitrogen stream. The apparatus is stoppered with cap 5 without lubricant, and with cap 6 with lubricant. The apparatus is disconnected from the apparatus and ground glass joint 7 stoppered with a cap fitted with a spiral capillary. When the distillation apparatus is not in use all the ground glass joints are stoppered with caps.

Thermostatting

Temperature is kept constant to an accuracy of ± 0.0005° by cutting down heat exchange with the surrounding medium to the minimum. The thermostat is a Dewar flask with a transparent surface fitted inside a plexiglass case (Fig. 6).

The operating thermostat is placed inside a large thermostat in which the temperature is maintained to an accuracy of ± 0.003° by means of a mercury-toluene thermoregulator.

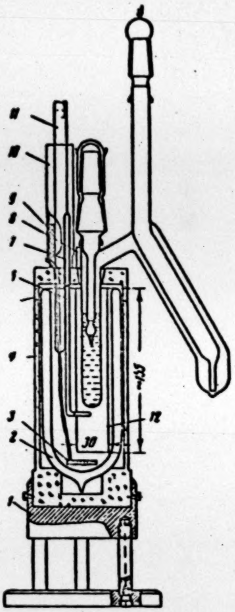

Fig. 6. Thermostat controlled to ± 0.0005°.
1) Support; 2) Dewar flask; 3) heater; 4) case; 5) case lid; 6) stirrer; 7) stirrer guide; 8) glass tube cooling the water; 9) stopper; 10) glass detail; 11) thermometer; 12) two gaps in the Dewar flask (silver removed).

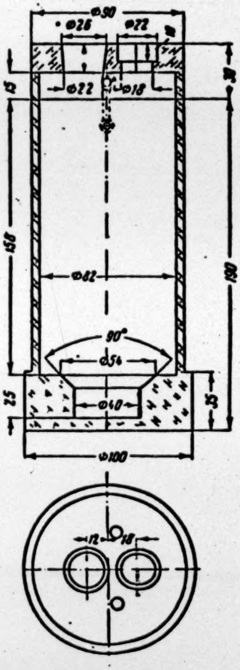

Fig. 7. Case for thermostat.

Five openings are drilled in the cover of the plexiglass case. The largest hole (d = 26 mm) is tapered; the conical part of the tube of the measuring apparatus fits into this. A glass detail 10 fits into the next opening (d = 22 mm), while a Beckmann thermometer fits through this detail; the latter is shown separately on Fig. 8.

In order to act as a shock absorber when the thermometer is lightly tapped, the latter is fitted into stopper 9 made of sponge rubber.

Openings (d = 6 mm) are arranged symmetrically at the sides of the thermometer. A glass tube serving as a guide for the stirrer is fitted into one of these openings. Tube 7 reaches down to the inner surface of the lid and is lifted clear of the water surface in the outer thermostat. The stirrer is vertically operated. Tube 8 is fitted into the other opening alongside the thermometer; its top end coincides with the level of tube 7, but it reaches almost to the bottom of the Dewar flask; water used for cooling is passed through this tube at a rate regulated by a three-way tap. A lead for supplying current at 12 volts to heater 3 is passed through the fifth hole which is a small one; the current is controlled with a rheostat. A source of illumination is placed behind the Dewar (Fig. 9); a 2 volt bulb can be moved up and down in this illuminator and is switched on when measurements are being made. More details of the construction and operation of this thermostat are given in monograph [3].

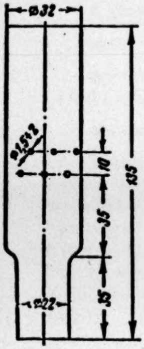

Fig. 8. Detail used for fixing the thermometer.

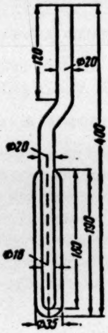

Fig. 9. Illuminator.

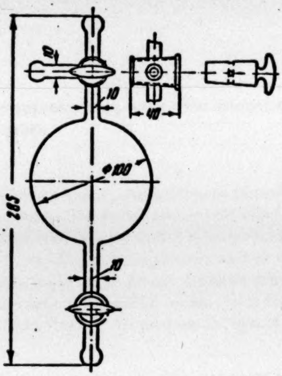

Fig. 10. Manostat.

Measurement of Equilibrium Flotation Temperature

The measuring apparatus filled with test water and closed with caps 9, 5, and 6 (the latter with lubricant) is placed in the thermostat as shown in Fig. 6, and the temperature in the outer thermostat adjusted (± 0.005°) to be the same as in the operating thermostat. The thermometers used in both thermostats were checked*. For centering the float a tube is fused into the upper part of the tube carrying the float; the former ends in a glass rod with a funnel shaped enlargement.

The rate at which the float moves is measured by means of a tube fitted with an ocular micrometer; the temperature is kept constant for 10 minutes after making a measurement. The float should not move at a rate faster than 0.3-0.4 divisions/second. Measurements should be carried out at no less than four temperatures differing from one another by 0.002-0.003°, under conditions when the float is rising as well as falling. The time taken for the float to shift over 2-5 divisions is measured with a stop watch. The equilibrium flotating temperature is established graphically. Cap 10 is fitted on instead of cap 9 after measurement is complete.

The apparatus is emptied by removing cap 10, carefully tilting the apparatus and transferring water from tube 1 into vessel 3, taking care that air does not get inside the tube. Polyvinylchloride tubing is introduced into vessel 3, the tube is connected to a vacuum pump and the water sucked out; about 40 ml is left as a seal.

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* A 2° Beckman thermometer is used in the operating thermostat; reading accuracy 0.0005°.

Application of Corrections

1. Correction for Changes in the Isotopic Composition of Water During Purification. Before each distillation a calculation is made of the amount of light fraction corresponding to 5% of the amount of sample taken for distillation, and it is assumed that the density of the water left behind has been increased by 0.08 γ. The amount of water left in the flask after distillation is expressed as a percentage of the amount distilled and the following decreases in density are assumed:

Residue in %:	2	4	6	8	10
Δd (γ):	0.03	0.09	0.14	0.19	0.23

Density changes which occur during four distillations are added up. As a result of the tailings which occur during tests, the water density decreases; consequently corrections are applied to the results, expressed in gammas, obtained after measurement.

2. Corrections for Beckmann Thermometer Readings.

a) Correction for the protruding column.

$\Delta = 0.00016 \cdot \Delta t \cdot l$, where Δt is the difference between room temperature and thermostat temperature; l – is the length of the protruding column of mercury in degrees.

b) Correction for changes in atmospheric pressure.

In order to find the corrections for changes in atmospheric pressure, the Beckmann thermometer fitted in a rubber stopper is placed in a wide test tube with an outlet tube. The tube which is half filled with water is connected to a vacuum pump and manometer, and the system tested to see that it is hermetically sealed; the test tube plus thermometer are then placed in a thermostat operating at a temperature near to the equilibrium flotation temperature of the float in standard water. Pressure is altered at 10 mm intervals over the range 720–770 mm using the manostat depicted on Fig. 10, and the thermometer readings noted. From these results the mean value of the correction to be applied to the thermometer readings for pressure changes of 1 mm is calculated.

3. Corrections for Changes in Float Readings with Atmospheric Pressure. The measuring apparatus is filled with standard water. The ground glass cap 8 with two branches (Fig. 4) is greased and fitted onto vessel 3 (Fig. 4). The equilibrium flotation temperature of the float is then measured in the standard water at atmospheric pressure, which is also measured. The measuring apparatus is connected by means of rubber tubing with the manostat (Fig. 10) and the equilibrium flotation temperature determined over a range of pressures differing by approximately 10, 20, and 30 mm from atmospheric pressure. During measurements, a note is made of room temperature and atmospheric pressure so as to be able to apply corrections for the thermometer readings. Float readings are reduced to the same pressure to which thermometer readings are related. When the pressure at which the equilibrium flotation temperature is determined in the test water is higher than the pressure chosen, the correction has a negative sign, while if the pressure is lower the correction has a positive sign.

An Example of the Application of the Corrections

It was found that the equilibrium flotation temperature of the float in standard water was 1.0535° according to the Beckmann thermometer. This corresponds to 24.3°. Measurements had been carried out at a room temperature of 19.5° and an atmospheric pressure of 741 mm. The level of the water in the inner narrow tube of the measuring apparatus was 25 mm higher than the level of the water in the wide tube; this corresponds to 2 mm of mercury; consequently, the pressure in the measuring vessel was 741 + 2 mm = 743 mm.

The correction for the projecting column in the Beckmann thermometer is therefore: 24.3–19.5° = 4.8°. A correction is therefore applied to the equilibrium flotation temperature 1.0535 + 0.0011 = 1.0546°.

We then reduce the measurement to a pressure of 755 mm, which is taken as standard.

Application of the correction for changes in thermometer reading. It was found that Beckmann thermometer readings changed by 0.00018° per mm change in pressure. Consequently in this particular case one must apply a correction corresponding to a difference in pressure of 755 – 741 mm = 14 mm. The change in temperature corresponding to this pressure change is 0.0025°. The corrected value is then: 1.0546 + 0.0025° = 1.0571°.

Correction for change in float readings. For a pressure change of 1 mm, it was found that the equilibrium flotation temperature changed by 0.00007°. A correction for 12 mm (755-743 mm) is therefore applied, i. e. a correction of 0.00007 × 12 = 0.00084°. The corrected value of the equilibrium flotation temperature is: 1.0571 + 0.0008 = 1.0579°.

On calculating the correction for changes in the isotopic composition of water during its purification, we find that the density of water changed by 0.40 γ. At 24.3° a change in temperature of 0.001° corresponds to a change in the density of water of 0.25 γ. Consequently, it is necessary to add 0.0016° to the last corrected value of the equilibrium flotation temperature. As a result of applying all these corrections we get a value of 1.0595° instead of 1.0535°, i. e., a difference of 0.006°.

Reproducibility of the Measurements

The reproducibility of measurements carried out by the method described above is evident from Table 1; this table also clearly demonstrates the necessity of applying corrections. Thus, the largest difference in the corrected values of the equilibrium flotation temperature of the float in standard water, prepared at different times, amounts to 0.0004°; this corresponds to 0.1 γ, while the differences in uncorrected values amount to 0.0072° (or 1.8 γ).

TABLE 1

Date of measurement	Water sample	Correction for fractionation	Room temperature, °C	Pressure on thermometer	Pressure on float	Equilibrium flotation temp (measured)	Equilibrium flotation temp. (corrected)
23.X	1	0.0011	24.0	768	767	1.0607	1.0590
31.X	1	0.0011	21.0	764	765	1.0598	1.0593
31.X	2	0.0008	21.0	758	758	1.0584	1.0592
10.XII	3	0.0010	19.5	741	743	1.0535	1.0591
10.XII	3	0.0010	19.5	741	743	1.0538	1.0594

TABLE 2

Date of measurement	Correction for fractionation	Room temperature, °C	Pressure on thermometer	Pressure on float	Equilibrium flotation temp (measured)	Equilibrium flotation temp. (corrected)
21.XII	0.0004	20.5	754	755	1.0355	1.0370
21.XII	0.0004	21.0	749	750	1.0341	1.0369
24.XII	0.0004	20.5	753	754	1.0345	1.0362

Table 2 contains results for the same sample of water kept over a period of several days in the measuring apparatus. The measurements show that the equilibrium flotation temperature remains constant, i. e. the water does not take up alkali from the Jena glass, while the water seal prevents external contamination from getting into the test sample.

We should like to thank E. A. Yakovleva for valuable advice.

SUMMARY

1) A flotation method of determining density differences is described which enables isotopic analysis of natural waters to be carried out with an accuracy of ± 0.0002 atomic % D or O^{18}.

2) A thermostat is described which enables the temperature to be kept constant with an accuracy of ± 0.0005°.

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A CONDUCTOMETRIC METHOD OF DETERMINING WATER HARDNESS BY MEANS OF COMPLEXONE III

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Methods have been published for the conductometric determination of various ions by means of Complexone III [1]. During determination of water hardness, both direct and back titration of test water with Complexone III have been tried, the titration end point being established on the basis of the color change of the appropriate indicator. Nevertheless, when the water is turbid or colored it is difficult to establish the color change, and sometimes it is quite impossible; as a result, complexometric determination of water hardness is not applicable in such cases. The conductometric technique described below can be used for determination of hardness in both turbid and colored waters. The method was worked out on synthetic mixtures made up from standard solutions of calcium and magnesium salts taken in various proportions; it has been tested on natural waters. As a control the hardness of natural waters was also determined by Varta-Pfeifer's method [2], and by means of a complexometric method [3], on the basis of instructions for determination of water hardness issued by the Volkov chemical factory.

In the conductometric method the hardness was determined by titration with Complexone III solution after addition of some ammoniacal buffer solution.

0.1 N Complexone III solution was used; this was prepared by dissolving 18.613 g of the marketed product in 1 liter of distilled water. If the solution obtained by dissolving Complexone III in water is turbid, it should be filtered. The solution obtained was standardized by conductometric titration with 0.01 N solution consisting of a mixture of calcium chloride and magnesium sulfate solutions taken in the proportion of 3 : 1 by volume. The mixed solution of calcium and magnesium salts was prepared by pipetting 7.5 ml of 0.1 N calcium chloride and 2.5 ml of 0.1 N magnesium sulfate into a 100 ml standard flask (taking into account correction for decinormality) and the volume made up to the mark with distilled water.

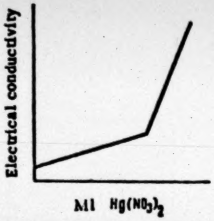
0.1 N calcium chloride was prepared by dissolving 5.005 g of chemically pure calcium carbonate dried at 110° in concentrated hydrochloric acid contained in a 1000 ml standard flask. The aliquot of carbonate was quantitatively transferred to the flask and a small amount of distilled water added; 5-9 ml of concentrated hydrochloric acid was then added. Residual calcium carbonate was dissolved by careful dropwise addition of hydrochloric acid, the reaction between carbonate and acid was allowed to finish before addition of the next drop of acid. When solution was complete the volume was made up to the mark with distilled water.

0.1 N magnesium sulfate was prepared from twice crystallized $MgSO_4 \cdot 7H_2O$; the concentration of the solution prepared was checked gravimetrically (the pyrophosphate method) [4].

Since the alkaline earth metals form stable complexes with Comprexone III at pH 10, titration was carried out in the presence of an ammoniacal buffer; the latter was prepared by mixing 1 N solutions of ammonium chloride and ammonium hydroxide in the proportion of 1 : 5 by volume [5].

The Complexone III solution was standardized as follows. 5 ml of the prepared 0.01 N mixture of calcium and magnesium salts was measured into the vessel used for conductometric titration which was fitted with a cylindrical piston stirrer [6]; 0.5 ml of ammoniacal buffer solution was then added, followed by distilled water in such amount that the volume of the solution being titrated was 50 ml. The solution was stirred and then conductometrically titrated with Complexone III solution; the latter was added by means of a pneumatic microburet [7]. The solution was thoroughly stirred after each addition of reagent. Titration was carried out on a setup of the Toropov type of conductometric apparatus [8].

A conductometric titration curve was constructed on the basis of the results obtained; the titration curves have the form shown in the diagram.



Interference from iron, aluminum, and other ions during indicator complexometric determination of water hardness has been pointed out in several papers. In order to study the effect of these ions on titration results, known amounts of aluminum as sulfate, or iron as chloride or Mohr's salt, were added to the solution to be titrated, and the final solutions conductometrically titrated as usual with Complexone III. Interference from aluminum became apparent at concentrations greater than 20 mg/liter (taking into account that a maximum of 10 ml of test water was used for titration). Iron did not interfere even at concentrations greater than 100 mg/liter.

In Lurye's article [9], it is indicated that aluminum in amounts less than 10 mg/liter and of iron less than 5 mg/liter do not interfere with hardness determination by back complexometric indicator titration. On addition of ammoniacal buffer solution to test water containing iron ions, ferric hydroxide is formed, which, being in a suspended state, colors the solution. The color which thus develops interferes with establishing the color change of the indicator.

During conductometric titration, formation of ferric hydroxide after addition of ammoniacal buffer solution to the test water does not affect experimental results.

Determination of the Hardness of Natural Waters by Various Methods

No. of the test water	ml water taken for analysis for conductometric	Hardness found, in degrees of German hardness		
		Conductometrically	Vart-Pfeiffer method	By the method in [9]
1	10	5.51	5.49	5.52
2	10	9.52	9.52	9.68
3	5	24.08	24.08	23.68
4	5	24.19	24.30	24.21
5	2	32.20	31.97	32.29
6	2	35.40	36.51	36.51
7	2	47.60	45.30	47.63

The following technique was used for determination of the hardness of natural waters: 2-10 ml of test water, depending on its hardness, was pipetted into the vessel used for conductometric titration; 0.5 ml of ammoniacal buffer solution was added and the volume made up to 50 ml with distilled water. The ammoniacal buffer should be added after the distilled water, otherwise, when test water is rich in magnesium the latter may be precipitated as magnesium hydroxide. When precipitates are formed, titration takes longer since the precipitate dissolves slowly.

The solution thus prepared was titrated conductometrically with Complexone III, the amount of the latter used for titration being established graphically from the titration curve. From the amount of Complexone III used, the hardness was calculated in milligram equivalents per liter, or in degrees hardness. The following formulas were used:

$$H = \frac{0.1 \cdot 1000 \cdot 2.8 \cdot K \cdot a}{V} = \frac{280 \cdot K \cdot a}{V}.$$

where H is the hardness; 0.1 is the normality of the Complexone III solution; K is the correction factor for the decinormality of the Complexone III solution; a is the volume (in ml) of Complexone III used for titrating the test water; V is the volume (in ml) of test water taken for titration; 1000 is the conversion factor for 1000 ml of test water; 2.8 is the correction factor for expressing water hardness in degrees of hardness (German).

For calculating water hardness in milligram equivalents the latter factor is omitted and the formula acquires the form:

$$H = \frac{100 \cdot K \cdot a}{V}.$$

The Table contains comparative results obtained during determination of the hardness of natural waters by the suggested method and by two other methods which are used in practice.

The results show that the conductometric method of complexometric titration is no less accurate than the other methods, namely the method described in [9] and the Vart-Pfeifer method. The advantage of the method we have presented is that when it is used, determination of water hardness is possible in turbid and colored waters; it is also faster. The small volume of test water required allows a determination to be carried out more rapidly, while in the case of series analyses, as a consequence of the decrease in amount of reagents used, cost of analysis also decreasese.

SUMMARY

A conductometric method has been developed for determining the hardness of turbid and colored water. The accuracy of the method is satisfactory.

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RAPID METHODS OF MICROELEMENTAL ANALYSIS

PART 14*. MICRODETERMINATION OF CARBON AND HYDROGEN IN ORGANOFLUORINE COMPOUNDS

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Determination of carbon and hydrogen in organofluorine compounds has been studied by many research workers to date. Investigations in elemental microanalysis have been carried out within the framework of the classical methods of Pregl and Friedrich, and have been directed towards overcoming the difficulties associated with the quantitative oxidation of organofluorine compounds and complete absorption of fluorine-containing products inside the combustion tube. Various reagents which have formed part of the packing of the combustion tube in addition to the usual oxidizing agents and platinum contacts have been tried as absorbers for fluorine [1-6]. During analysis of highly fluorinated hydrocarbons and carbon fluorides, it has been recommended that combustion temperature be increased, and that combustion should be carried out in a stream of moist oxygen [2, 7-9]. The latter makes determination of hydrogen impossible; in this connection, determination of hydrogen in organofluorine compounds has been specially considered, but has not hitherto been solved satisfactorily [4, 8, 10, 11].

In developing a method for determining carbon and hydrogen in materials containing fluorine, we tried to make it as reliable as the method used for analysis of the usual materials. The basis of our method was pyrolytic combustion in a rapid stream of oxygen [12, 13]; this technique has been successfully used in many microanalytical laboratories in Russia, and recently abroad [14, 14a]. During pyrolytic combustion of organofluorine compounds the fluorine can be quantitatively held back in the decomposition zone of the test aliquot by an "internal absorbent", which is packed into the quartz tube used for decomposition of the material [15]. The "internal absorbent" may be a material which is stable at about 1000° and which can be converted into a non-volatile, high melting fluoride and a readily decomposed carbonate. Magnesium oxide is the material which satisfies these requirements most closely:

	MgO	MgF_2	$MgCO_3$
Melting point	2800°	1125°	Starts to decompose at 300°
Boiling point	3600°	2260°	

Pyrolytic combustion in the presence of magnesium oxide for absorption of fluorine opens up various possibilities of simultaneous determination of carbon, hydrogen, and fluorine [15, 16]. The simplest method would be to determine the fluorine content approximately on the basis of the change in weight of the tube containing magnesium oxide in which pyrolytic decomposition had been carried out. This variant is applicable to materials which are free from other elements which are trapped by magnesium oxide. In accordance with the equation $MgO + 2F = MgF_2 + {}^1/_2O_2$, absorption of 38 weight units of fluorine would lead to a change in weight of the absorbent of only 22 weight units; e. g. during combustion of 7.6 mg of material containing 50% fluorine, an error in weighing the tube containing magnesium oxide of 22 γ would lead to an error in fluorine determination of 0.5% (absolute). In practice the fluorine content found may deviate from the theoretical value by as much as a few percent. Nevertheless, in a number of cases, a knowledge of the approximate fluorine content may be important; consequently, in the present article, in addition to determination of carbon and hydrogen, we have also described the variant in which all three elements are determined on one aliquot.

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* For Part 13 see J. Anal. Chem. 12, 424, (1957). [See C.B. translation.]

TABLE 1*

Name and formula of test material	Weight in mg	Found, in %: C	Found, in %: H	Difference, %: C	Difference, %: H
2,4-Dinitrophenylhydrazone of trifluoropropiophenone	5,025	48.76	2.88	-0.16	—0.13
C—48,92%; H—3,01% $C_{13}H_{11}F_3N_4O_4$	5.432	48.79	2.98	—0.13	—0.03
The amide of α-hydroperfluoropropionic acid	5.960	24.81	2.06	—0.01	—0.03
C—24,82%; H—2,09% $C_3H_3F_4NO$	5.060	24.84	2.10	+0.02	+0.01
The anilide of α-hydroperfluoroisobutyric acid	4.307	44.23	2.60	—0.06	—
C—44,29%; H—2,60% $C_{10}H_7F_6NO$	5.100	44.35	2.65	+0.06	+0.04

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* Analysis carried out by A. S. Lapteva

Another variant for the simultaneous determination of carbon, hydrogen, and fluorine which is based on the pyrohydrolysis of the magnesium fluoride formed during determination of carbon and hydrogen [16] seems to us to have greater possibilities.

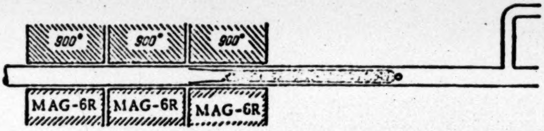

Fig. 1.

The expediency of using magnesium oxide for absorption of fluorine during elemental analysis is confirmed by the work of other investigators, who have used magnesium oxide, or preparations based on it, under the conditions used in classical microanalysis as a component part of the packing used in the combustion tube; it has been used in conjunction with cupric oxide and metallic silver [6], with lead dioxide, cupric oxide, metallic silver [3], or with metallic silver, lead oxide, lead dioxide, in the form of eight alternate layers[5]. In every instance it can be stated that magnesium oxide is a better absorbent for fluorine than anything else which has been used for this purpose previously in elemental analysis; it is superior, for example, to lead oxides, lead chromate, sodium fluoride, potassium fluoride, etc.

The method, in essence, consists of sprinkling test material together with magnesium oxide into a quartz tube, and subjecting it to pyrolytic combustion in an empty combustion tube in an oxygen stream. The fluorine is thereupon trapped by the magnesium oxide, while carbon and hydrogen are determined as usual [12, 13]. The magnesium oxide must be conditioned beforehand. When other halogens are present in the test material they are absorbed by metallic silver which is placed in the combustion tube and is heated to 550-600° [17]; nitrogen oxides are trapped outside the combustion tube by means of dry absorbents [18]; sulfur, phosphorus, boron, silicon, and metals (apart from the alkali and alkaline earth metals) do not interfere with determination of carbon and hydrogen, but remain in the magnesium oxide layer with the fluorine. In substances containing only C, H, O, N, and F, the latter can be determined approximately at the same time as carbon and hydrogen from the changes in weight of the tube containing the magnesium oxide.

TABLE 2

Name and formula of test material	Weigh in mg	Found, in %: C	Found, in %: H	Found, in %: F	Difference, in %: C	Difference, in %: H	Difference, in %: F
Methyl α-hydroperfluoroisobutyrate $C_5H_4O_2F_6$ C — 28.58% H — 1.92% F — 54.27%	8.086 5.015	28.64 28.55	1.96 1.91	55.96 60.88	+0.06 -0.03	+0.04 -0.01	+1.69 +6.61
Ethyl α-hydroperfluoroisobutyrate $C_6H_6O_2F_6$ C—32.15% H—2.70% F—50.87%	11.670 8.021	32.12 32.15	2.76 2.83	51.50 50.40	-0.03 —	+0.06 +0.13	+0.63 -0.47
Methyl-β-hydroperfluoroisobutyl ether $C_5H_4OF_8$ (b.p. 70°) C—25.87% H—1.74% F—65.50%	7.342 10.374	25.84 25.81	1.63 1.78	68.45 63.84	-0.03 -0.06	-0.11 +0.04	+2.95 -1.66
Methyl perfluoroisobutenyl ether $C_5H_3OF_7$ (b.p. 90°) C—28.31% H—1.43% F—62.71%	11.532 4.542	28.38 28.55	1.61 1.65	60.83 64.68	+0.07 +0.24	+0.18 +0.21	-1.88 +1.97
The amide of α-hydroperfluoropropionic acid $C_3H_3ONF_4$ C—24.82% H—2.08% F—52.39%	8.117 8.641 8.178	24.78 24.67 24.75	2.35 2.16 2.11	52.86 51.47 54.85	-0.04 -0.15 -0.07	+0.27 +0.08 -0.03	+0.47 -0.98 +2.46
The diethylamide of α-hydroperfluoroisobutyric acid $C_8H_{11}ONF_6$ (m.p. 51°) C—38.25% H—4.41% F—45.38%	11.708 8.508	38.41 38.43	4.41 4.55	46.33 47.09	+0.16 +0.18	— +0.14	+0.95 +1.71
The anilide of α-hydroperfluoroisobutyric acid $C_{10}H_7ONF_6$ C—44.29% H—2.60% F—42.04	5.730 6.062	44.45 44.59	2.66 2.67	43.46 43.34	+0.16 +0.33	+0.06 +0.07	+1.42 +1.30
α-Hydroperfluoropropionic nitrile C_3HNF_4 (b.p. 41°) C—28.36% H—0.79% F—59.82%	9.680 8.411	28.59 28.30	0.84 0.94	61.02 —	+0.23 -0.06	+0.05 +0.15	+1.20 —
Diethylperfluoroisobutenylamine $C_8H_{10}NF_7$ C—37.95% H—3.98% F—52.53%	6.795 16.234	38.00 37.78	3.98 4.12	56.20 52.67	+0.05 -0.17	— +0.14	+3.67 +0.14

On the basis of the results for combustion of non-volatile, high melting fluorine-containing compounds, we became convinced that fluorine is absorbed in a thin layer of magnesium oxide during pyrolytic decomposition of the test sample. Table 1 contains the results of analyses carried out in a tube 6.5 cm long containing a layer of magnesium oxide 5 cm long. Depending on the volatility of test material, decomposition starts at various distances from the bottom of the tube, so that the length of the magnesium oxide layer required for quantitative trapping of the fluorine changes accordingly. Consequently, on carrying out series analyses of materials whose structure and properties are unknown, it is necessary to increase the length of the magnesium oxide layer appreciably. According to our observations, even during combustion of liquids boiling at 35-40°, a 12-13 cm layer of MgO is quite sufficient. When it is necessary to carry out an approximate determination of fluorine alongside carbon and hydrogen determination, combustion of the test material is carried out in a long quartz tube (15 cm) filled with magnesium oxide, and placed in an empty combustion tube (Fig. 1). In this way it is possible to analyze various materials including low boiling liquids containing more than 70%

TABLE 3

Name and formula of test material	Weight, in mg	Found, in %		Difference, in %	
		C	H	C	H
1,1,1-Trifluoro-2-bromo-3-trichloro-acetoxypropane $C_5H_3BrCl_3F_3O_2$ C—17.75% H—0.89% F—16.84%	10.370	17.80	0.87	+0.05	—0.02
	12.640	17.88	0.91	+0.13	+0.02
Perfluorodiethylmethylamine $C_5F_{13}N$ (b. p. 45°) C—18.71% F—76.93%	9.334	18.60	0.20	—0.02	+0.20
	8.685	18.59	0.24	—0.12	+0.24
Perfluorotriethylamine $C_6F_{15}N$ (b.p. 70°) C—19.42% F—76.80%	10.360	19.57	0.17	+0.15	+0.17
	11.063	19.69	—	+0.24	—
Ethyltrifluoroacetate $C_4H_5F_3O_2$ C—33.81% (b. p. 70°) H—3.55% F—40.11%	9.223	34.00	3.66	+0.19	+0.11
	10.697	33.74	3.57	—0.07	+0.02
Diethyl-β-fluoroethylphosphinate $C_6H_{14}FO_4P$ C—36.00% H—7.05% F—9.49%	6.970	36.00	7.03	—	—0.02
	6.290	35.93	6.97	—0.07	—0.08
o-Ethyl-S-β-fluoroethyl ester of methylphosphinic acid $C_5H_{12}FOPS$ C—32.25% H—6.50% F—12.85%	6.060	32.29	6.53	+0.04	+0.03
	6.818	32.46	6.66	+0.21	+0.16
β-Fluoroethyl paranitrophenyl ester of methylthionphosphinic acid $C_9H_{11}FO_4NPS$ C—38.71% H—3.97% F—6.80%	7.698	38.58	3.98	—0.13	+0.01
	5.816	38.50	4.06	—0.21	+0.09
2,2-Diphenylenedioxonium boron fluoride $C_{18}H_{13}BF_4O$ C—65.12% H—3.95% F—22.88%	9.444	65.14	3.97	+0.02	+0.02
	8.328	65.31	4.08	+0.19	+0.13
Diphenylchloronium boron fluoride $C_{12}H_{10}BClF_4$ C—52.12% H—3.65% F—27.49%	7.981	52.09	3.71	—0.03	+0.06
	7.793	52.15	3.90	+0.03	+0.25
Diphenylbromonium boron fluoride $C_{12}H_{10}BBrF_4$ C—44.92% H—3.15% F—23.68%	8.560	44.97	3.12	+0.05	—0.03
	6.460	44.93	2.95	+0.01	—0.20
β-Chlorovinylphenyliodonium boron fluoride $C_8H_7BClF_4I$ C—27.28% H—2.00% F—21.57%	7.490	27.26	2.02	—0.02	+0.02
	7.666	27.13	1.99	—0.15	—0.01

fluorine (See Table 2). When it is only necessary to determine carbon and hydrogen, another variant is better; in this variant combustion is carried out in a short tube filled with magnesium oxide, this tube in turn being placed in a hollow quartz sleeve (Fig. 2) containing the same absorbent. The magnesium oxide in the sleeve is placed there with the object of trapping small amounts of fluorine which are not trapped in the tube itself; this additional magnesium oxide can be used without changing it during the whole of a working day, while that in the tube itself should be changed for each determination. Using this sleeve it is possible to carry out determinations considerably more quickly than when a long tube on its own is used, and far less magnesium oxide has to be used. Results for determinations in which this second variant was used are given in Table 3.

Apparatus

A standard apparatus* for microdetermination of carbon and hydrogen is necessary for carrying out an analysis[13]; the following are required in addition:

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* The complete apparatus is produced by the "Laborpribor" factory in Klin.

1. When carbon and hydrogen are to be determined in fluorine-containing materials:

a) a hollow quartz sleeve with a sintered bottom;

b) quartz tubes for the samples

The sleeve should readily fit into the combustion tube, while the quartz tube for the sample, in turn, should easily fit into the sleeve, so that there is a gap of about 2 mm between tube and sleeve. This gap is necessary so that during combustion enough oxygen can get into the sleeve. When a standard combustion tube s used, the external diameters of sleeve and tube should be 8-8.5 and 5-6 mm respectively. All the same it s more difficult to carry out pyrolytic combustion in a narrow tube than in the usual type of tube; consequently, we recommend the following dimensions for the combustion tubes, sleeves, and tubes for the sample, as being more convenient:

	Length in mm	Diameter in mm	
		External	Internal
Combustion tube	500	13.5	11.5
Sleeve	200	10	8.5
Tube for sample	65 - 90	7	5.5

c) an MA-14 open electric oven 14 cm long, operating at 900°.

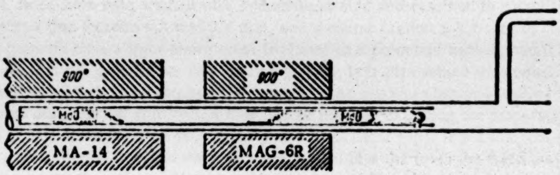

Fig. 2.

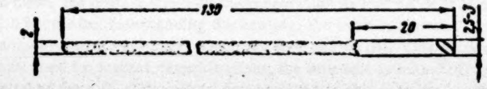

Fig. 3.

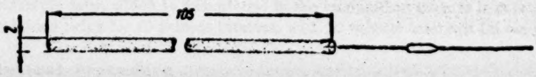

Fig. 4.

2. When carbon, hydrogen, and fluorine are to be determined simultaneously:

a) quartz tubes for the samples 150 mm long and 8-9 mm in diameter, fitted with ground glass stoppers]. The surface of the sample tube should be faultless;

b) quartz scoops for introducing aliquots of solid test material into the sample tube (Fig. 3);

c) quartz rods for pushing capillaries containing test material into the sample tubes when the material is liquid (Fig. 4);

d) two MAG-6R electric ovens operating at 900°, length 6 cm;

3. For conditioning magnesium oxide:

a) a gas holder and the usual purifying system for oxygen*;

b) ampoules made from high melting sample tubes for storing the conditioned magnesium oxide;

c) an MA-O_2-20oven operating at 1150°, length 20 cm.

Conditioning the Magnesium Oxide

Air dry magnesium oxide contains considerable amounts of water and carbon dioxide at room temperature, and it gradually gives these up on heating. Magnesium oxide loses its hygroscopicity after calcining at 1600° and higher; at the same time, however, it loses its chemical activity [19], and such a preparation becomes inert even towards fluorine. In the temperature range we are interested in, namely 800-1000°, the change in the absorptive properties of magnesium oxide on increasing the temperature becomes so significant that it might be the source of large errors in the elemental analysis. This makes it essential to condition any magnesium oxide to be used as an internal absorbent for fluorine.

We tested magnesium oxide in the form of dust, granules, and preparations deposited on a carrier. The best method proved to be deposition of magnesium oxide on pumice, which is readily strewn into the sample tube, hardly corrodes quartz at all and has no tendency to form dust. The pumice used was material which had been ground, freed from dust, washed with hydrochloric acid and calcined in a muffle [20]. It is convenient to use two fractions; a fine fraction down to 0.5 mm, and a coarse faction 1-1.5 mm in cross section. The calcined pumice whose granules have a light brown color is placed in a porcelain beaker, and is lightly moistened with distilled water (so that the granules do not stick together); it is then mixed with powdered magnesium oxide. 0.5 g of magnesium oxide is taken per gram of pumice. The mixture obtained is dried to a friable state when it is sieved free from dust. An old combustion tube can be used for calcining the preparation; the end of such a tube is cut and is ground at an angle of 45°. A lump of ashless filter paper is put into this tube, the purpose of the filter being to keep the granules in place when they are loaded into the tube; the dried preparation is loaded into the tube and the oxygen throughput adjusted to 30-40 ml per minute; the tube is fitted into a cold oven so that the filter is outside the oven limits, while all the magnesium oxide is inside. When the oven is allowed to warm up, too rapid combustion of the filter should be avoided; otherwise some of the preparation may be expelled from the oven. The required temperature (1100-1150°) is reached in the course of 20-30 minutes. When the filter paper has been burnt, the oven is fitted on the preparation so that all of it is calcined at a temperature of not less than 1100°; 1.5 hours after commencing the heating, the oven is removed, and the calcined preparation transferred to glass ampoules with long necks which are then sealed off. One ampoule containing about 1.5 g of the preparation can be used for several determinations; the ampoule is sealed off immediately after some of the preparation has been taken from it. The preparation obtained in this way has a white color with a slight yellow tinge. The oxygen used for this conditioning is purified in the same way as that used for actual combustion during analysis.

When carbon, hydrogen, and fluorine are determined simultaneously, granulated magnesium oxide without a carrier is used; it is conditioned immediately before analysis. The calcined preparation is strewn into a long quartz sample tube, which is then placed in the combustion tube; it is calcined with three electric ovens at 900°; it is calcined twice for 10 minute intervals with 10 minute intervals for cooling between each calcination.

Analytical Procedure

a) Determination of Carbon and Hydrogen

The setup normally used for carbon and hydrogen is mounted [12, 13], the electric ovens are switched on, and absorption apparatus containing anhydrone and askarite connected; some of the coarse fraction of the preparation of magnesium oxide on pumice is poured through a funnel with a long stem into the sleeve until $^1/_3$ of its length is packed with the preparation; the sleeve as a whole is slipped into the combustion tube while the aspirator tap is closed; some of the fine fraction of the preparation is then loaded into the quartz sample tube, and the latter placed in the sleeve and its position adjusted inside the sleeve such that all the magnesium oxide is within the zone heated to 900° by MA-14 and MAG-6R ovens. Two sample tubes are used for each determination; magnesium oxide is calcined in one of them prior to combustion; the other takes the sample. A blank is carried out in the course of 15-20 minutes at an oxygen throughput of 20 ml/ minute; the absorption apparatus is disconnected and prepared for weighing (wiping and discharging any electrical charges); the end of the combustion tube is covered and the oven used for heating the sleeve withdrawn. The absorption apparatus is weighed and connected to the setup, the aspirator tap,however,being kept closed; an aliquot of test sample is introduced into a quartz sample tube. The sleeve is moved on to the open end of the combustion tube, the tube containing the calcined magnesium oxide is withdrawn and some of the latter is strewn over the sample in the sample tube; the latter is then replaced in the sleeve. The sleeve and the sample in its tube are moved into the combustion tube to occupy the same position used for the blank; the magnesium oxide in the sleeve is heated with an MA-14 oven, the oxygen flow is switched on (20 ml/ minute) and pyrolytic decomposition of test material is commenced by placing a gas burner or electric oven under the open end of the sample tube; the burner is then moved forward in a direction opposite to the oxygen flow. The arrangement of the sleeve and sample tube in the combustion tube is shown in Fig. 2. During combustion of liquids, the sample is introduced in a sealed capillary into the empty sample tube; magnesium oxide is then strewn into the tube and the hair fine end of the capillary broken against the bottom of the sample tube by pressing on the other end of the capillary which sticks out with a tweezers. When the liquid is nonvolatile there is no need to seal the capillary.

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* If the apparatus used for C and H determinations is only used periodically, then use can be made of its purifying system; the latter is connected to the tube used for conditioning after the combustion tube, or connected in parallel with it.

Most compounds liberate carbon during pyrolysis, so that the analyst, by observing the formation of a dark coating on the magnesium oxide,can readily regulate the rate of combustion. Normally, combustion takes 10-15 minutes, but volatile liquids which decompose with carbonification must be burned more slowly (15-20 minutes). During analysis of materials boiling below 50°, it is recommended that the part of the sample tube where the sample itself is located be cooled with dry ice after introduction of the sample. After combustion it is essential to calcine the sleeve along the whole of its length with ovens MA-14 and MAG-6R for 10 minutes, in order to decompose magnesium carbonate formed, after which the absorption apparatus is disconnected from the setup and weighed. A fresh portion of magnesium oxide is strewn into a clean sample tube, the used sample tube is removed from the sleeve and replaced by the new one. While weighing is in progress the sleeve is heated along the whole of its length by electric ovens for 15 minutes, oxygen being passed through the apparatus during the heating. The absorption apparatus is connected to the setup, the ovens are withdrawn, the next test aliquot is taken and the analysis of the fresh sample carried out as already described. The satisfactory operation of the setup is checked by carrying out combustion of a pure fluorine-containing compound and the respective corrections applied for the weight of CO_2 and H_2O. If the test material contains other halogens in addition to fluorine, the former are not held back by magnesium oxide completely [16]; accordingly, in such a case, a platinum contact 3-4 cm long is inserted between the sleeve and the outlet of the combustion tube; the platinum contact is heated with the same oven as that used for heating the sleeve. After the platinum contact a layer of metallic silver 4-5 cm is inserted; this is heated with an electric oven to 550-650°. Sulfur, boron, phosphorus, silicon, and metals (apart from the alkali and alkaline earths) are held back in the sample tube by magnesium oxide in addition to fluorine, and do not interfere with the determination. One determination takes 60-70 minutes.

b) Simultaneous Determination of Carbon, Hydrogen, and Fluorine

When the blank is carried out, a long quartz sample tube containing conditioned magnesium oxide without carrier is introduced into an empty combustion tube; it is then calcined with three electric ovens for two ten minute periods as indicated above. The absorption apparatus is disconnected, after which sample tube plus magnesium oxide are withdrawn; it is stoppered with a ground glass stopper and placed on a long metal block near the balance. The absorption apparatus is weighed; it is then connected immediately to the setup, the aspirator tap being kept closed. Sample tube plus magnesium oxide are weighed 30 minutes after their removal from the combustion tube. When the test material is solid it is introduced by means of a small quartz scoop into the sample tube; the scoop is tapped gently so that the sample falls far enough into the tube for the latter to be stoppered after combustion. Liquid test materials are introduced in capillaries into the sample tube by means of a quartz rod. If the capillary has had to be fused then the fused end has to be broken against the bottom of the sample tube. Sample tube plus sample are finally placed in the combustion tube, the tap of the aspirator is opened and an oven fitted onto the open end of the sample tube so that not less than 3-4 cm of MgO is within the heating zone. Two other electric ovens are fitted onto the tube in addition to the first; towards completion of combustion the whole of the magnesium oxide layer is heated with the ovens. When combustion is complete, the tube is calcined as described above, and then weighing carried out. When using magnexium oxide in a quartz apparatus it must be borne in mind that test material and the quartz surface are readily electrified during movement of sample tubes along the combustion tube. It is recommended that electric charges be removed by passing those parts of the apparatus liable to pick up such charges through a burner flame.

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SUMMARY

1. It has been established that during rapid pyrolytic combustion at 900° of organo-fluorine compounds in a layer of magnesium oxide contained in a quartz apparatus, quantitative oxidation of highly fluorinated compounds and complete retention of fluorine can be achieved using only a short length of magnesium oxide.

2. A microanalytical method has been developed for determination of carbon and hydrogen in organo-fluorine compounds (solid and liquid, including volatile liquids) containing nitrogen, halides, sulfur, boron, phosphorus, silicon, and metals not forming carbonates which are difficult to decompose.

3. Another variant is suggested for analysis of materials containing carbon, hydrogen, oxygen, nitrogen, and fluorine, whereby, in addition to determining carbon and hydrogen, it is possible to get an approximate value for the fluorine content.

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* [Russian translation.]

** [See C.B. translation.]

QUANTITATIVE DETERMINATION OF ACETIC ANHYDRIDE

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Acetic anhydride is widely used in organic synthesis, mainly as an esterifying agent, but also in other cases. Accurate determination of the acetic anhydride content, both in the raw materials and in finished products, is of essential importance if the synthesis is to be carried out successfully. Existing methods for its determination can be divided into the following groups:

1. Determination of the acetic acid obtained during interaction of acetic anhydride with water or alkali. The method is only suitable for a two component system, since calculations are made on the assumption that total acetic anhydride plus acetic acid amounts to 100%. The error in such an indirect determination may be significant.

2. Methods based on formation of acetanilides

$$(CH_3CO_2)O + C_6H_5NH_2 \rightarrow C_6H_5NH(COCH_3) + CH_3COOH.$$

First suggested by Menshutkin and Vasilyev [1] as long ago as 1889, the method consists in titrating the acetic acid obtained in two separate tests – in the first as the result of formation of acetanilide, and in the second as a result of the hydrolysis of acetic anhydride by water.

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH.$$

Subsequently, various other aniline derivatives were used in this method: m-nitraniline, p-nitraniline, dichloraniline. Acetic anhydride content is determined either on the basis of the difference in titration of the acetic obtained in the two separate tests, or on the basis of the excess aniline or its derivatives by titration with sodium nitrite solution. The projected new GOST method for acetic anhydride includes this method of Menshutkin and Vasilyev, modified somewhat by introduction of a catalyst – pyridine – during hydrolysis of acetic anhydride with water.

3. Methods based on simultaneous use of hydrolysis and acylation reactions:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH;$$
$$(CH_3CO)_2O + CH_3OH \rightarrow CH_3COOCH_3 + CH_3COOH.$$

Lukashevich [3], who suggested this method, carried out both reactions by heating in the absence of catalysts; free acids do not interfere with anhydride determination.

Smith and Bryant [4] modified this method by using pyridine as a catalyst for both reaction, and titrating the acetic anhydride directly with sodium methylate solution:

$$(CH_3CO)_2O + CH_3ONa \rightarrow CH_3COOCH_3 + CH_3COONa.$$

Both reactions rapidly reach the end point at room temperature. Under the experimental conditions used acetic acid does not react with methanol, so that it is possible to determine the anhydride in the presence of free acid. At low concentrations, however, the results are not accurate.

Nicolas and Burel [5] have shown that instead of using sodium methylate for the esterification reaction, it is possible to carry out a direct titration of acetic anhydride with a solution of sodium hydroxide in methanol:

$$(CH_3CO)_2O + CH_3OH + KOH \rightarrow CH_3COOK + CH_3COOCH_3 + H_2O,$$

in this way it is possible to avoid manipulating sodium metal. All the methods just mentioned which are based on formation of acetanilides and on acylation are not direct methods for determination of acetic anhydride, but require two separate titrations. The amount of acetic anhydride is calculated by difference.

4. Individual Methods. Of other methods suggested for determination of acetic anhydride, mention may be made of a method based on decomposition of the anhydride by anhydrous oxalic acid in the presence of anhydrous pyridine [2], according to the equation:

$$(COOH)_2 + (CH_3CO)_2O \rightarrow CO + CO_2 + CH_3 + CH_3COOH.$$

The amount of acetic anhydride is determined either from the volume of gases liberated, or by titration of excess oxalic acid with potassium permanganate. The following physical methods, while being more rapid, are less accurate:

1) a thermometric express method for anhydride determination in mixtures with acetic acid, based on elevation of the temperature during reaction with acetanilide [6];

2) determination of the setting point of acetic acid obtained as a result of hydrolysis of acetic anhydride [7];

3) an approximate method based on the solubility of acetic acid [8].

The methods listed require, as already indicated, either a double determination (methods based on formation of acetanilides, or on acylation) or do not give sufficiently accurate results.

Methods based on decomposition of acetic anhydride with water and determination of the amount of the latter consumed can be regarded as the most accurate methods for direct determination of acetic anhydride.

Under normal conditions at room temperature, and in the absence of catalysts, the reaction between acetic anhydride and water proceeds very slowly; it can be accelerated by heating or by addition of catalysts either acidic or basic in character. The mechanism of the reaction which occurs between acetic anhydride and water in the presence of pyridine can be represented as follows:

$$\begin{gathered}(CH_3CO)_2O \rightarrow CH_3CO^+ + CH_3COO^- \xrightarrow{Py} CH_3COOPy + CH_3CO^+ \xrightarrow{H_2O} \\ \rightarrow CH_3COOH + CH_3COOHPy,\end{gathered}$$

i. e. dissociation into the anion CH_3COO^- and the cation CH_3CO^+ occurs. In the presence of such catalysts as pyridine, the anion combines with the latter to form CH_3COOPy, while the liberated cation CH_3CO^+ reacts with the hydroxyl ion to give acetic acid. In the presence of acid catalysts it is possible that an intermediate compound CH_3COR' (R' is the acid radical of the catalyst) is formed; this intermediate compound then gives acetic acid with the proton H^+ thereby regenerating the catalyst.

Elevation of the temperature undoubtedly favors dissociation of acetic anhydride. Smith, Bryant, and Mitchell have suggested two methods for determining acetic anhydride which do not involve use of acidimetric titration. One of these methods is based on acid hydrolysis under the influence of boron trifluoride [9], while the other, which has had wide application, is based on hydrolysis in a pyridine solution using sodium iodide as catalyst [10]. In both cases the amount of water which reacts is determined when hydrolysis is complete by titration with Karl Fischer reagent.

These authors state that when only pyridine is used, hydrolysis of other anhydrides, apart from acetic anhydride, does not usually go to completion even in those cases where water is present in 100% excess in the reaction medium. Better results are obtained, in their opinion, when stronger organic bases than pyridine are used as catalysts; such bases are tributylamine, triethylamine, and n-butylamine. The exception is acetic anhydride, which in the presence of a large excess of water of about 100% gives quantitative results in the presence of pyridine. On the assumption that methods based on hydrolysis of acetic anhydride and measurement of excess water are the most suitable for analysis of acetic anhydride, we investigated methods involving alkali and acid hydrolysis. We found that acetic anhydride is hydrolyzed quantitatively in the presence of pyridine, without using NaI as catalyst (and in the presence of a small excess of water).

The necessary conditions for the reaction to proceed quantitatively are: approximately double the amount of pyridine, excess water – 20-25%; a temperature of 60-70°, and a reaction time of half an hour.

Instead of using boron trifluoride during acid decomposition, we tried a solution of water in acetic acid containing a small amount of H_2SO_4 (0.2-0.3%). It was found that under these conditions acetic anhydride hydrolyzes very rapidly event at room temperature, while hydrolysis in the presence of BF_3 required two hours heating and large excess of catalyst.

The possibility of carrying out determinations at room temperature simplifies analysis appreciably, since it does not require closed flasks for heating and enables loss of water to be avoided. The conditions which we have established are described in detail below.

The use of this last method enabled us to detect the very interesting fact of the coexistence in glacial acetic acid of acetic anhydride and water; this can be explained by the equilibrium:

$$2CH_3COOH \rightleftarrows H_2O + (CH_3CO)_2O.$$

Direct titration of glacial acetic acid with Karl Fischer reagent (very rapid titration) indicated that it contained water; determination of acetic anhydride both by means of acid catalysis (H_2SO_4) and alkaline catalysis (pyridine) showed that acetic anhydride was also present. To illustrate this graphically we quote the following results: sample No. 1 of acetic acid contained 0.22% of water and 1.59% of acetic anhydride. On addition of catalyst (H_2SO_4) the water content dropped to zero, while the acetic anhydride content dropped to 0.3%; 0.22% of water corresponds approximately to 1.25% of acetic anhydride so that the residual acetic anhydride should be 0.33%; the amount found, as already stated, was 0.3%. Acetic acid sample No. 2 contained 0.1% water and 2% acetic anhydride. After hydrolysis in the presence of sulfuric acid the residual acetic anhydride was 1.4%. The water content of 0.1% corresponds to 0.57% acetic anhydride; the calculated residual acetic anhydride is therefore 1.43% as against the 1.40% actually found.

It is sufficient for determination of acetic anhydride in acetic acid to determine the water content of the latter before and after addition of 0.2-0.3% of sulfuric acid to the acetic acid. A decrease in water content will indicate the presence of acetic anhydride.

For our work in studying the methods of determining acetic anhydride we used acetic anhydride chemically pure grade, which contained 97%; determination was carried out by means of a GOST method based on formation of acetanilide. By fractional distillation on a column we succeeded in increasing its content by 1%.

Determination of Acetic Anhydride in the Presence of Pyridine

Reagents required: pyridine chemically pure; Fischer reagent.

An aliquot of acetic anhydride (about 1.5-2 g) was introduced into a 50 ml round bottom flask with a long neck and containing 3-4 ml of pyridine; the necessary amount of water calculated on the basis of a 20-25% excess with respect to the anhydride was then added rapidly (for speeding up weighing of the pyridine and acetic anhydride it is more convenient to measure them out with automatic pipets). The flask was then connected to a reflux condenser fitted with a ground glass joint and heated for half an hour; the flask was placed on an electric sand bath at such a distance that a thermometer placed alongside the flask at the level of the liquid indicated a temperature of 60-70°; A blank test using pyridine was carried out at the same time. On finishing heating the flask was allowed to cool without separating it from the condenser; the contents were then titrated with Fischer reagent.

The results were calculated by means of the formula:

$$\%\ \text{acetic anhydride} = \frac{102[a-(b-c)d]\cdot 100}{18 \times H} = \frac{5.67[a-(b-c)d]\cdot 100}{H}$$

where a is the weight of water; b is the number of milliliters of Fischer reagent used for the test sample; c is the number of milliliters of Fischer reagent used in the blank test; d is the titer of Fischer reagent expressed in grams of water; W is the weight of acetic anhydride taken.

Table 1 contains results of determinations of acetic anhydride in the presence of pyridine for various heating times and reaction temperatures.

TABLE 1

Results of Determinations of Acetic Anhydride in the Presence of Pydidine at Various Temperatures and Heating Periods

No. of test	Weight taken		Reaction time	Reaction temperature	Excess Water, %	Anhydride found, %	Notes
	Anhydride in g	Water in g					
1	1.6041	0.3212	2 hours	Room temp.	20	93.3	Anhydride, "Pure" grade (97%)
2	1.6205	0.3245	6 »	»	17.7	95.2	
3	1.5986	0.3400	1 »	50°(Water bath)	52.5	95.9	
4	1.5945	0.3174	1 »	50 »	19.5	94.8	
5	1.6032	0.3259	30 min	60—70° (Air heating)	19.0	97.1	
6	1.6326	0.3280	30 »	60—70° »	17.0	97.3	
7	1.5947	0.3375	30 »	60—70° »	22.0	97.34	
8	1.6024	0.3315	60 »	60—70° »	20.0	97.3	
9	1.5884	0.3357	60 »	60—70° »	22.5	97.6	
10	1.6239	0.3248	30 »	60—70° »	15.7	98.0	Twice distilled acetic anhydride
11	1.6195	0.3153	30 »	60—70° »	12.8	97.75	
12	1.6223	0.3834	60 »	60—70° »	36.7	98.0	

TABLE 2

Effect of the Amount of Pyridine

No. of test	Weight taken		ml of pyridine	Anhydride in %
	Anhydride in g	Water, in g		
1	1.6193	0.3083	2	97.3
2	1.5792	0.3275	3.5	97.4
3	1.6048	0.3223	7.0	97.4

The amount of pyridine used does not have an essential effect, as can be seen from Table 2.

Table 3 contains results of analysis of synthetic mixtures of acetic anhydride and acetic acid, in the presence of pyridine.

TABLE 3

Results of Analysis of Synthetic Mixtures of Acetic Anhydride and Acetic Acid in the Presence of Pyridine (Acetic Anhydride 97%)

No. of test	Weight taken			Excess water found in g	Acetic anhydride, in %	
	Acetic anhydride, g	Acetic acid, g	Water, g		Taken	Found
1	1.0343	0.3317	0.2001	0.0250	73.5	72.6
2	1.0580	0.4307	0.2430	0.0629	68.6	68.3
3	1.0686	0.5323	0.2380	0.0555	64.7	64.6
4	1.2602	1.2161	0.2557	0.0691	49.4	49.5
5	0.5145	1.1433	0.1035	0.0153	30.2	30.7
6	0.3522	1.1524	0.0842	0.0252	22.04	22.2

Determination of Acetic Anhydride Using Sulfuric Acid as Catalyst

Necessary reagents: acetic acid containing 0.3-0.6% of water, 0.2-0.3% of H_2SO_4 sp.gr. 1.84; Fischer reagent.

1-1.5 g of acetic anhydride was introduced into a ground neck flask; for small amounts of anhydride the aliquot can be increased. 8-10 ml of acetic acid containing 0.2-0.3% of sulfuric acid was then added, followed by the amount of water required to decompose the acetic anhydride taken; the amount of water taken should be 20-25% in excess of theory. After allowing the mixture to stand for five minutes at room temperature (not less than 18-20°) it was titrated with Fischer reagent after thorough agitation; a blank was carried out in parallel, using the same amount of the acetic acid reagent containing 0.2-0.3% of H_2SO_4. Results were calculated as for the previous method.

TABLE 4

Results of Determination of Acetic Anhydride in Synthetic Mixtures by means of Two Methods: 1) In the presence of H_2SO_4; 2) In the presence of Pyridine

Aliquots taken		Acetic anhydride, in %		
			Found	
Mixture in g	Water in g	Taken	Method 1	Method 2
1.2117	0.2089	97.0	97.04	97.05
1.3471	0.1630	48.5	48.0	48.4
1.4706	0.0830	24.5	24.05	25.0
3.2508	0.030	5.0	5.2	5.4
3.4500	0.045	2.5	2.3	2.7
3.374	0.040	1.0	0.9	0.95

Table 4 contains results for determination of acetic anhydride in synthetic mixtures by means of the two methods: the first involving H_2SO_4, the second using pyridine.

SUMMARY

1. Methods of determining acetic anhydride which are based on its hydrolysis, with subsequent determination of the amount of water consumed, are the most accurate and simple methods for determining this compound;

by means of such methods it is possible to determine acetic anhydride in multicomponent systems.

2. Hydrolysis of acetic anhydride proceeds quantitatively rapidly enough in the presence of catalysts, both basic (pyridine), and acid in character (boron trifluoride, sulfuric acid).

3. A method is suggested for determination of acetic anhydride which is based on hydrolysis in the presence of sulfuric acid at room temperature, excess water being titrated with Karl Fischer reagent.

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DETERMINATION OF CARBOXYLIC ACID AMIDES BY SAPONIFICATION

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Methods for the quantitative determination of amides have not been sufficiently developed. Some of the work carried out along these lines during the last 25 years has been devoted, for the most part, to determination of primary amides.

It has been recommended that acetyl derivatives of aromatic amines be determined by boiling them with a solution of KOH in benzyl alcohol (b.p. 205°), with subsequent back titration with hydrochloric acid using phenolphthalein as indicator [1]. It was suggested later [2] that it should be possible to determine primary carboxylic acid amides by saponification over a period of several hours with a 10% solution of KOH in benzyl alcohol, with distillation of the ammonia formed into standard acid. This method was developed in detail by Rovira [3], who used diethylene glycol (b.p. 244°) and glycerol (b.p. 290°) as well as benzyl alcohol, as solvents. The use of such high boiling solvents enables the saponification time to be cut down to 1 hour (in the case of the primary amides of the simplest carboxylic acid amides). A variant of the saponification method which is suitable for working with the amides of non-volatile bases and which does not require distillation of the base has been suggested by Olsen [4]. His method involves saponification by boiling with 1 N KOH in ethylene glycol for 6 hours followed by titration of the reaction mixture with aqueous hydrochloric acid using a Methyl Orange type of indicator, chosen in accordance with the extent of dissociation of the organic base formed. The increase in alkalinity in comparison with a control test, as a result of liberation of free bases during saponification of the amides, is equivalent to the amount of saponified amide.

Some amides are saponified under much milder conditions than those indicated above. Thus, a 15 minute boil with 12% sulfuric acid is sufficient for quantitative hydrolysis of adipic acid amides [5].

The amount of ammonium salts formed in this case was determined by the formol method.

The following methods have been suggested as methods of determining amides apart from the saponification method: dehydration to their nitriles, conversion to the hydroxamic acids, and reduction to amines.

Dehydration of amides to give nitriles by moderate heating with 3,5-dinitrobenzoyl cloride [6] is only suitable for primary amides, and can be used for their determination in the presence of secondary and tertiary amides.

On heating with hydroxylamine, amides are converted into hydroxamic acids RCONHOH, which form colored salts with trivalent iron, and can in this way be determined colorimetrically [7].

Quantitative reduction of amides to amines under mild conditions is only possible with such strong reducing agents as lithium aluminum hydride.

This method was suggested not long ago [8] for analysis of amides; its advantage is that it makes it possible to determine tertiary amides which cannot be dehydrated to nitriles, and are very difficult to saponify.

The aim of the work described here was to make a study of the possibility of determining carboxylic acid amides by saponification; in particular, determination of secondary and tertiary amides, the compounds least studied by previous investigators. The method which we wish to put forward does not require distillation of the amine formed during saponification; it is based on the property of aliphatic amines noted previously by

Menshutkin [9] of not changing the color of indicators of the phenolphthalein type in alcohol solutions. Thus, on titration of the reaction mixture obtained after alcoholic alkali saponification of the amides, with an alcoholic acid solution, it is possible to observe a decrease in the amount of alkali

$$RCONR_2 + OH^- \rightarrow RCOO^- + NHR_2 \qquad (1)$$

just as is the case during saponification of esters:

$$RCOOR + OH^- \rightarrow RCOO^- + ROH \qquad (2)$$

EXPERIMENTAL

Materials Used. Pure preparations of 13 liquid amides: the formamide, N-alkyl, and N,N-dialkylamides of formic, acetic, and butyric acids, used in the work have already been described previously [10].

Acetamide (m.p. 79.5-82°) and acetanilide (m.p. 115.5°) were obtained by recrystallization of the commercial products from alcohol.

Saponification was carried out with 0.2-1 N solutions of chemically pure potassium hydroxide in rectified spirit and in commercial ethylene glycol. The aliquot of amide (4-10 mg.mole.) was placed in a 100 ml round bottom flask made from alkali resistant glass•; 20 or 25 ml of the potassium hydroxide solution was then added by pipet. When viscous glycol-solutions were used the pipet was held vertically for 5 minutes for the liquid to run off the glass. The mixture was boiled under reflux. Duration of boiling was varied in the preliminary experiments from 1 to 6 hours in order to establish the optimum conditions.

On cooling, the excess of alkali was titrated with a solution of acetic acid in rectified spirit. The normality of the acid corresponded roughly to that of the alkali used for saponification••.

During saponification with alcoholic alkali, back titration was carried out visually with thymolphthalein (several drops of 0.1% alcoholic solution).•••

During saponification with ethylene glycol solutions of alkali the reaction mixture was often observed to turn dark, so that titration with a color indicator was difficult. In such cases we used potentiometric titration with a Haber glass electrode and an amplifier using "Zhelud 954" tubes.

In view of attack by boiling alkali solutions on glass, it is absolutely essential to carry out blanks under identical conditions, but without the amide.

Percentage of saponified amide (p) was calculated by means of the formula:

$$p = \frac{(V - v)NM}{10m}, \qquad (3)$$

where V and v are the number of milliliters of acetic acid solution used for titrating the blank and the test solution respectively; m is the weight in mg of test material; N is the normality of the acetic acid solution; M is the molecular weight of the amide.

• From glass No. 23. Pyrex flasks were found unsuitable.

•• The factor of the alcoholic solution of acetic acid drops on keeping as a result of esterification, so that it is necessary to check it periodically.

••• Phenolphthalein can also be used as indicator, but the color change is not so clear.

RESULTS AND DISCUSSION

Preliminary tests showed that the rate of saponification of secondary and tertiary amides, just like that of primary amides, depends on the nature of the corresponding acid. Furthermore, the saponification rate depends to a considerable extent on the number and the nature of the substituents on the nitrogen atom. In view of this it seemed inexpedient (and impossible) to use the same technique for all amides. On the basis of a large number of experiments we have developed two variants for analysis.

Variant A. This is meant for determination of comparatively readily saponifiable amides, and consists in boiling an aliquot of test material, corresponding to 5 mg. moles of amide, with 20 ml of 0.5 N alcoholic potassium hydroxide for 1.5-2 hours, followed by subsequent titration with 0.5 N alcoholic acetic acid, using thymolphthalein as indicator.

Variant B. (This variant is used for amides which are difficult to saponify). It consists of boiling an aliquot containing about 8-10 mg. mole of amide with 20 ml of 1 N potassium hydroxide in ethylene glycol for 3-4 hours. The excess alkali is potentiometrically titrated with alcoholic acetic acid using a glass electrode.

Under the conditions used in Variant A, formamide and its nearest homologs – methylformamide, dimethylformamide, and ethylformamide, – are completely saponified.

TABLE 1

Determination of Readily Saponifiable Amides by Means of Variant A (Boiling with 0.5 N alcoholic alkali)

Amide	Boiling period, in hours	Weight taken, in g	Amide found		Experimental error, in %
			in g	in %	
Formamide	1.5	0.1885	0.1877	99.6	—0.4
Formamide	1.5	0.2002	0.1986	99.2	—0.8
Methylformamide	1.5	0.1833	0.1849	100.9	+0.9
Methylformamide	1.5	0.1964	0.1978	100.7	+0.7
Methylformamide	1.5	0.3359	0.3331	98.3	—1.7
Dimethylformamide	2	0.3604	0.3598	99.8	—0.2
Dimethylformamide	2	0.2980	0.2991	100.4	+0.4
Dimethylformamide	2	0.2861	0.2838	99.2	—0.8
Ethylformamide	2	0.3710	0.3691	99.5	—0.5
Ethylformamide	2	0.3474	0.3445	99.2	—0.8
n-Butylformamide	2.5	0.7254	0.7200	99.2	—0.8
n-Butylformamide	2.5	0.6248	0.6255	100.2	+0.2
n-Butylformamide	2*	0.4043	0.4051	100.2	—0.2

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* Concentration of the alcoholic KOH 0.94 N

As can be seen from Table 1 which only contains a small number of the results we obtained, these amides can be determined with an accuracy of up to 1%.

The higher, secondary formamides (n-butylformamide) require more stringent saponification conditions – 1 N alkali instead of 0.5 N. It is much more difficult to saponify the higher tertiary formamides. Diethylformamide, for example, is only saponified to the extent of 29-35% after 2 hours with 0.5 N alcoholic alkali; for its complete saponification it must be boiled with alkali in ethylene glycol as in Variant B. Variant A is not applicable to amides of acetic acid and its homologs. As our experiments showed, acetamide and dimethylacetamide are only saponified to the extent of 40-50% after a two hour boil with 0.5 N alcoholic KOH. Complete saponification of such amides with alcoholic alkali takes such a long time that the use of Variant A becomes inconvenient.

Under the conditions used in Variant B, primary and secondary amides of acetic acid and its homologs are saponified completely (see Table 2). Furthermore N, N-dimethylamides are completely saponified, but tertiary amides with heavier radicals are saponified much more slowly. We did not succeed in saponifying di-n-butylbutyramide even after 6 hours boiling with 1 N KOH in ethylene glycol.

TABLE 2

Determination of Amides which are Difficult to Saponify – Variant B – (Boiling with 1 N KOH in Ethylene Glycol)

Amide	Boiling period, in hours	Weight taken, in g	Amide found		Experimental error, in %
			in g	in %	
Diethylformamide*	3	0.2974	0.2989	100.5	+ 0.5
Diethylformamide*	3	0.3552	0.3461	97.4	— 1.6
Acetamide	3	0.7343	0.7259	99.8	— 0.2
Acetamide	3	0.6720	0.6614	98.4	— 1.6
Ethylacetamide	4	0.7434	0.7371	99.2	— 0.2
Ethylacetamide	4	0.7496	0.7415	98.9	— 1.1
Dimethylacetamide	2	0.5575	0.5575	100.0	± 0.0
Dimethylacetamide	2	0.5789	0.5704	98.5	— 0.5
Dimethylacetamide	4	0.7005	0.7047	100.6	+ 0.6
Dimethylacetamide	4	0.6806	0.6804	100.0	+ 0.0
n-Butylbutyramide	4	0.9758	0.9750	99.9	— 0.1
n-Butylbutyramide	4	1.0959	1.0858	99.1	- 0.9
Acetanilide	3	1.0612	1.0581	99.7	— 0.3
Acetanilide	3	1.2623	1.2524	99.2	— 0.8
n-Butylbutyramide	4	1.0795	1.0821	100.2	+ 0.2
n-Butylbutyramide	4	0.9689	0.9580	98.9	— 1.1
Dimethylbutyramide	4	1.0662	1.0648	99.9	— 0.1
Dimethylbutyramide	4	0.9869	0.9829	99.6	— 0.4
Di-n-butylbutyramide	6	0.8397	0.5006	59.6	—40.4
Di-n-butylbutyramide	6	1.1484	0.6154	53.6	—46.4

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* Titration was carried out visually using thymolphthalein as indicator

TABLE 3

Determination of Dimethylformamide, by Saponification, in the Presence of Nitrosamine, Diethylacetamide, and Di-n-butylbutyramide (Variant A)

Second component of test mixture	Weight of sample taken		Dimethylformamide found by saponification	
	Dimethylformamide in g	Second component, g	in g	in %
Dimethylnitrosamine	0.1930	0.4805	0.1894	98.13
Dimethylnitrosamine	0.3032	1.3668	0.3013	99.37
Diethylnitrosamine	0.4120	0.9626	0.4085	99.15
Diethylacetamide	0.3688	0.3112	0.3645	98.83
Diethylacetamide	0.4121	0.3427	0.4085	99.12
Di-n-butylbutyramide	0.3501	0.4598	0.3499	99.94

Further increases in the duration of the boiling time, increases in alkali concentration, and the use of solvents boiling at even higher temperatures, in order to get complete saponification of higher tertiary amides when the recommended variant is used, are undesirable on account of the increase in errors which are the outcome of attack on the glass by alkali.

Consequently, Variant B is not suitable for determining certain higher tertiary amides which are difficult to saponify.

All the same, in a number of cases, the method suggested is more simple and more convenient than saponification methods suggested earlier [3, 4] for primary and secondary amides, and also for N, N-dimethylamides. The variant which we have described is particularly suitable for formamide and dimethylformamide which are of considerable industrial importance.

An advantage of the method suggested is the fact that it is suitable for determination of amides in the presence of free amines.

When mixtures contain amine salts or free acids, it is necessary to apply a correction for the amounts of these present; this is readily done by a preliminary titration of an aliquot of test material with alcoholic alkali, using thymolphthalein as indicator*.

Esters which are saponified by alkali interfere with determination of amides by the method described, and should be absent**. Nitriles are saponified appreciably under the conditions used in Variant A and accordingly interfere with determination of amides.

Nitrosamines (amides of nitrous acid) and the higher tertiary amides (apart from N, N-dimethylamides) are, on the other hand, hardly saponified at all by alcoholic alkali. Consequently, it is possible to determine formamides in the presence of nitrosamines and higher tertiary amides; this is very important in certain special cases. Examples of such determinations are given in Table 3.

SUMMARY

1. A method has been developed for determination of carboxylic acid amides by saponification which does not require distillation of the amines formed. Two variants have been worked out: the first involves the use of alcoholic alkali for readily saponifiable amides of formic acid; the second variant is based on the use of an ethylene glycol solution of potassium hydroxide for primary and secondary amides carboxylic acid which are difficult to saponify, and also for N, N-dimethylamides. The accuracy of the method is 1% of the value being measured.

2. The method described is not suitable for determination of certain higher tertiary amides which can only be saponified with great difficulty (presumably because of steric hindrance).

3. The large difference in the rates at which the simplest formamides and tertiary amides of other acids saponify can be made use of for determining formamide in the presence of nitrosamines and higher tertiary amides.

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* In alcoholic solution amine salts titrate like acids.

** The methods suggested earlier for determination of amides by saponification [3, 4], assume that esters are present.

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DETERMINATION OF MICROGRAM AMOUNTS OF ANILINE, METHYLANILINE, AND DIMETHYLANILINE IN THEIR MIXTURES

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Methods for the determination of microgram amounts of methylaniline in the presence of aniline and dimethylaniline, and the separate determination of these amines, are of importance for solving questions connected with the toxicity of the vapors of mixtures of amines, e.g. extralin, for studying contamination of tap water and the atmosphere in places of work. Methods have been published for the determination of small amounts of aniline [1-8], methylaniline and dimethylaniline [6, 9-12]; the methods proposed for the latter have been based on the rather slow [13], and non-specific [9, 14], nitrosation reaction. The techniques used for technical analysis of mixtures of aromatic amines [15-19] are not always applicable to microchemical methods.

Below are given the results of the study of a photometric method for separate determination of microgram amounts of the amines in their mixtures, in solution and in air. The work was carried out on an FMS photometer. For determination of aniline we used azo coupling of phenyldiazonium acetate with α-naphthol which ensures quantitative yield of the dye [8, 20], solutions of which have an orange-red color.

Dimethylaniline was determined by coupling with m-nitrophenyldiazonium to form an orange colored dye [15].

For determination of methylaniline, use was made of a reaction noted previously [21], namely the reaction between the oxidation products of methylaniline and phenol, which is accompanied by formation of blue colored solutions. Aniline behaves in similar fashion; in this case, however, the color of the solutions is connected with formation of indophenol [22]. The mechanism of the action of various oxidizing agents and the indophenol reaction have been discussed in the literature [22-25].

EXPERIMENTAL

For our work we used chemically pure aniline, dimethylaniline, and methylaniline; the latter contained up to 2% of aniline and dimethylaniline.

Experiments were carried out at concentrations of amines in air stored in cylinders or obtained by evaporation of synthetic ethereal solutions, as well as with solutions containing 10-50 μg/ml in water or dilute alcohol, prepared on the day of analysis from concentrated solutions (2 mg/ml) kept for 1-2 months.

Azo coupling of the diazotized aniline with α-naphthol is best carried out in an alkaline-ammoniacal medium at pH 11.5. Nevertheless the ammonia must be carefully controlled in such work, since if it is allowed to act for more than 1 minute the intensity of the colored solution decreases. For eliminating interference from dimethylaniline, which forms yellow solutions of the nitroso compound, photometric measurements were made using a 533 mμ light filter.

As a result of the small solubility of the dye, coupling of dimethylaniline with m-nitrophenyldiazonium is best carried out in concentrated alcoholic solution at pH 4.7-5.1.

For determination of methylaniline (aniline) Chloramine B was used successfully as an oxidizing agent instead of Chloramine T [26-27]. For coupling the oxidation products of methylaniline (aniline), best results were obtained at 22-30°, a chloramine concentration of 16-64 mg, sodium hydroxide 6-12 mg, phenol 12-24 mg in 4 ml of solution. The colored solutions maintain a linear relation between color intensity and amine concentration, under conditions where the action of chloramine is restrained by addition of sodium thiosulfate.

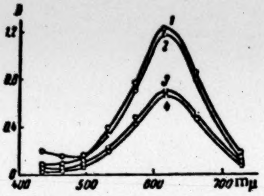

Fig. 1. Light absorption of solutions in relation to wave length (λ) : 1 and 3) aniline concentrations of 29 and 16 μg; 2 and 4) methylaniline concentrations of 42 and 24 μg in 4 ml.

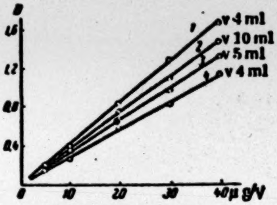

Fig. 2. Calibration curves: 1 and 4) aniline and methylaniline during coupling of their oxidation products with phenol; 2) dimethylaniline; 3) aniline during azo coupling with α-naphthol.

Maximum light absorption of the colored solutions obtained during coupling of the oxidation products of aniline or methylaniline with phenol is found at 619 mμ (Fig. 1), while the optical density of mixtures of such solutions is additive (Table 1). When the method indicated above is used for determining aniline, the facts just stated mean that it is possible to establish conditions for determination of methylaniline in amine mixtures. Below is described the technique used for analyzing solutions, and mixtures of air and amine vapors, for their content of individual components.

TABLE 1

Optical Density of Solutions Obtained by the Interaction of Solutions of the Oxidation Products of Aniline, Methylaniline, and Their Mixtures With Phenol (D = optical density)

Taken					Found		
Aniline		Methylaniline			D for solutions of amine mixtures	Deviation	
μg	D_1	μg	D_2	$D_1 + D_2$		absolute	in %
0.5	0.02	38.0	1.04	1.06	1.03	−0.03	−3.0
1.0	0.04	29.0	0.80	0.84	0.86	+0.02	+2.3
2.0	0.08	22.0	0.61	0.69	0.67	−0.02	−1.5
4.0	0.16	17.5	0.48	0.64	0.64	±0.00	±0.0
10.0	0.42	9.0	0.25	0.67	0.69	+0.02	+3.0
14.0	0.59	7.0	0.19	0.78	0.76	−0.02	−2.6
19.5	0.81	1.7	0.04	0.85	0.87	+0.02	+2.5
29.0	1.20	1.0	0.02	1.22	1.22	±0.00	±0.0
38.0	1.57	0.0	0.00	1.57	1.58	+0.01	+0.6

Determination of Aniline. To 2 ml of test solution acidified with 0.1 ml of 40% acetic acid is added 0.3 ml of reagent containing 20 mg sodium nitrite and 35 mg sodium bromide and the mixture diazotized for 5 minutes. 0.2 ml of 10% ammonia solution is added, the solution is then coupled within one minute of addition of the ammonia with 0.25 ml of α-naphthol dissolved in 0.5 ml of alcohol, and 0.1 ml of 40% sodium hydroxide solution is added. The solution is made up to 5 ml with 96% ethanol. During this procedure, as in subsequent determinations, the solution is thoroughly mixed before addition of reagent. After 10 minutes the solution is measured photometrically in a 1 cm cell using a 533 mμ filter. There is a linear relation between light absorption of the solution and aniline concentration (Fig. 2). By means of this method it is possible to determine 1-40 μg of aniline in 2 ml of the original solution with an average error of 6% (Table 2).

TABLE 2

Individual Determination of Amines in 10-15 ml of Solution

Aniline			Dimethylaniline			Methylaniline		
Taken, in μg	Found, in μg	Error, in %	Taken, in μg	Found in μg	Error, in %	Taken, in μg	Found, in μg	Error, in %
1.3	1.32	+1.5	1.3	1.2	−7.7	1.25	1.5	+20.0
1.3	1.4	+7.7	6.0	6.4	+6.7	1.25	1.7	+36.0
1.3	1.4	+7.7	31.0	29.0	−6.5	1.25	1.6	+28.0
2.6	2.8	+7.7	30.2	29.1	−3.7	2.5	2.8	+12.0
3.85	4.2	+8.5	4.1	4.0	−2.5	30.0	29.1	−3.0
5.45	5.2	−4.6	30.5	28.0	−8.2	10.0	11.0	+10.0
7.7	7.7	±0.0	5.3	5.2	−1.9	5.0	5.2	+4.0
10.5	9.4	−10.5	10.5	10.5	±0.0	10.0	9.2	−8.0
12.5	12.0	−4.0	50.0	45.0	−10.0	12.5	13.0	+4.0
25.0	26.0	+2.0	50.0	45.0	−10.0	25.0	22.5	−10.0
30.1	28.7	−6.0	2.65	2.6	−3.8	2.5	2.7	+8.0
38.0	34.5	−9.0	325.0	293.0	−10.0	178.0	165.0	−8.0
Mean		—	6.0	—	6.0	—	—	13.0

The method enables one to carry out a rapid determination of the amount of aniline in aqueous or alcoholic solutions of technical methylaniline or dimethylaniline (Table 3).

Determination of Dimethylaniline. To 4 ml of solution acidified with 0.1 ml of 15% acetic acid is added, in order to eliminate interference from primary and tertiary amines, 25 mg (2 drops) of acetic anhydride, 1 ml of 10% sodium acetate solution, and 0.35 ml of reagent prepared by mixing solutions of 25 mg of m-nitroaniline in 20 ml of 20% acetic acid and 4 ml of 1% sodium nitrite solution. The solution is made up to 10 ml with 96% ethanol. After 10 minutes the solution is measured photometrically in a 2 cm cell using a 465 mμ filter. Beer's law is obeyed at concentrations of 1-40 μg in 10 ml (Fig. 2).

By means of this method it is possible to determine 1 μg of dimethylaniline in 4 ml of test solution with an average error of 6% (Table 2). This method can be used for determining dimethylaniline in technical aniline or methylaniline.

TABLE 3

Determination of Aniline in Technical Methylaniline (Mean results for 2-5 determinations)

Weight of methyl-aniline, in g	Specified content of aniline, in %	Aniline found	
		in g	in %
0.248—0.99	4.0	0.0107—0.040	4.1
0.094—0.75	5.3	0.0052—0.041	5.5
0.090—0.72	5.6	0.0060—0.041	5.8
0.082—0.65	6.1	0.0040—0.034	5.2
0.075—0.60	6.7	0.0050—0.037	6.5
0.069—0.56	7.2	0.0050—0.040	7.1
0.065—0.52	7.7	0.0045—0.036	7.0
0.200—0.40	8.5	0.0160—0.032	8.0

Determination of Methylaniline (Aniline). To 2 ml of solution is added 0.9 ml of 15% ethanol and the mixture oxidized for 5 minutes with 0.5 ml of 6% Chloramine B solution stored for a month. 0.1 ml of 0.1 N sodium thiosulfate is then added, followed by 0.1 ml of 6% sodium hydroxide, and coupling carried out with 24 mg of phenol dissolved in 0.4 ml of water. After 20 minutes the solution is measured photometrically in a 1 cm cell using a 619 mμ filter. The sensitivity of the method is 1 μg of methylaniline (aniline) in 2 ml of test solution; the mean error of a determination is 13% (Table 2).

When aniline is also present this method gives total primary and secondary amines. The amount of methylaniline can be calculated by means of the calibration curves (Fig. 2), on the basis of the difference between two determinations: total content of primary and secondary bases, and aniline content as found by azo coupling with α-naphthol.

Dimethylaniline only affects determination of small concentrations of methylaniline (aniline) of the order to 4-6 μg in a test sample (Table 2).

The method described is suitable for determination of methylaniline in technical products.

For determining the content of aromatic amine vapors in air the latter is drawn at the rate of 1 liter/minute through 3 absorption flasks fitted with porous discs and containing 5 ml of 1% ethanol in each. The absorption solution in the last flask is acidified with 0.3 ml of 40% acetic acid. The vapors of aniline and methylaniline are absorbed in the first two flasks, while the dimethylaniline is absorbed in all three. The solutions in the first and second flasks are analyzed for their aniline and methylaniline contents. Equal amounts of solutions from the three flasks are combined and analyzed for their dimethylaniline content. An analysis takes 1 hour.

These methods which have been developed for the individual determination of amines have been used in sanitary-hygiene and experimental toxicological studies on the contamination of the air of industrial establishments, and studies on leather coatings, working clothes, and on the toxic properties of extralin vapors.

SUMMARY

1. Photometric methods are suggested for determining microgram amounts of methylaniline, and for separate determination of aniline, methylaniline, and dimethylaniline, in solution and in air. The bases of the methods for determining aniline and dimethylaniline are the coupling reactions with α-naphthol and m-nitrophenyldiazonium, respectively; for methylaniline (aniline), the suggested reaction is coupling of their oxidation products with phenol. The sensitivity of the method is 1 μg of amine while the experimental error is 6-13%.

2. Vapors of aromatic amines are absorbed with 1% ethanol by drawing the air at the rate of 1 liter/minute through three absorption flasks.

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A CRYOSCOPIC METHOD FOR THE QUANTITATIVE DETERMINATION OF UNSULFONATED IMPURITIES IN ARENES (AROMATIC HYDROCARBONS)

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The content of unsulfonated impurities has been normalized for a series of industrial products (benzene, toluene, xylene, pyrobenzene). This defines the practical value of the method for determining unsulfonated impurities. Quantitative determination of unsulfonated impurities is also of great importance in research work for fuller characterization of individual aromatic hydrocarbons and their mixtures; e.g. when aromatic hydrocarbons are used as components of synthetic mixtures; during development and checking of methods for the quantitative determination of this group of hydrocarbons; during checking of the purity of aromatic hydrocarbons isolated by the chromatographic method, etc.

The existing volumetric method for the quantitative determination of unsulfonated impurities in aromatic hydrocarbons [1] may prove insufficiently accurate in a number of cases (for more details see the experimental part). For a series of products which are viscous, semisolid and solid in consistency (e.g. for high molecular weight aromatic hydrocarbons isolated from lubricating oils, naphthalene, anthracene, etc) the volumetric method cannot, in general, be used for quantitative determination of unsulfonated impurities in aromatic hydrocarbons.

The disadvantages of the volumetric method enumerated compelled us to develop the cryoscopic method described below for determination of unsulfonated impurities in aromatic hydrocarbons in the presence of a solvent.

In principle the quantitative determination of unsulfonated impurities in aromatic hydrocarbons can be regarded as a special case of the quantitative determination of aromatic hydrocarbons, namely when the aromatic content of the test mixture is high, e.g. greater than 95%. Accordingly, for the quantitative determination of unsulfonated impurities in aromatic hydrocarbons, it is possible to use the cryoscopic method described previously in detail [2] for the quantitative determination of aromatic hydrocarbons in the presence of cyclohexane as solvent.

The method consists essentially of the following: to cyclohexane with a known crystallization point is added about 5 mole % of the test aromatic hydrocarbon and the crystallization temperature of the solution determined (t_1). The latter is treated with concentrated sulfuric acid until all the aromatic hydrocarbon has been removed. The crystallization temperature (t_2) of the product which is left is then determined. The content of unsulfonated impurity in the test aromatic hydrocarbon, in mole % (x), is then calculated from the equation (1):

$$x = \frac{100\,(t - t_2)}{t - t_1} = \frac{100\,\Delta t}{\Delta t_1}, \tag{1}$$

where t is the crystallization temperature of the original cyclohexane; t_1 is the crystallization temperature of the mixture (1) of cylcohexane to which test hydrocarbon has been added; t_2 is the crystallization temperature of mixture (1) after treatment with sulfuric acid until the aromatic hydrocarbon has been completely removed; Δt is the depression of the crystallization temperature of cylcohexane caused by the presence of the unsulfonated impurity, i. e. $\Delta t = t - t_2$; Δt_1 is the depression of the crystallization temperature of cyclohexane caused by addition of the test aromatic hydrocarbon, i.e. $\Delta t_1 = t - t_1$.

As shown in article [2], the mean accuracy of this method is 0.6% (mole).

The accuracy of the cryoscopic method for quantitative determination of unsulfonated impurities depends to a considerable extent both on the accuracy with which Δt can be determined, and also on the concentration of the test aromatic hydrocarbon in the cyclohexane solution. For a certain accuracy in measuring the depression Δt, the absolute accuracy of the quantitative determination of unsulfonated impurities depends mainly on the concentration of test aromatic hydrocarbon in the cyclohexane, as long as one does not take into account the variations in the value of "a" for cyclohexane (for more details on this point see below). Using equation (3) given below, and assuming that the absolute accuracy for measurement of the value of Δt is equal to 0.04° under our experimental conditions, we find that the absolute accuracy of determination of unsulfonated impurities depends mainly on the concentration of the aromatic hydrocarbon in the cylcohexane solution (in mole %): at an aromatic hydrocarbon concentration of 3%, the calculated accuracy for quantitative determination is 0.5%; for an aromatic hydrocarbon concentration of 10%, the accuracy is 0.1%; while for an aromatic hydrocarbon content of 50%, the accuracy is 0.02%.

In the work described here, the variant of the cryoscopic method for quantitative determination of unsulfonated impurities in the presence of a solvent was checked at an aromatic hydrocarbon concentration in the cyclohexane solution of about 50% (mole). Under these conditions the technique used for quantitative determination of unsulfonated impurities can be described briefly as follows.

An aliquot of test aromatic hydrocarbon is mixed with an aliquot of cyclohexane whose crystallization temperature has been determined beforehand. The aliquots are taken in such proportions that the content of test hydrocarbon in the cyclohexane solution amounts to about 50% (mole); they are weighed to an accuracy of 1 mg. The mixture is treated with concentrated sulfuric acid until the aromatic hydrocarbon has been completely removed. Under these conditions the unsulfonated impurities contained in the test aromatic hydrocarbon is not removed by the sulfuric acid, but remain in the cyclohexane solution whose crystallization temperature is accordingly depressed by Δt degrees. The content of unsulfonated impurities in the cyclohexane is equal to $\frac{\Delta t}{2.42}$% (mole), since in dilute solutions (up to 5%) each molar percent of the impurity will, as a rule, depress the crystallization temperature of cyclohexane by 2.42°.

The content of the unsulfonated impurities in the test hydrocarbon is calculated, in the general case, by means of equation (2):

$$x = \frac{100 \cdot a \cdot M\,\Delta t}{b \cdot M_1 (100 \cdot a - \Delta t)} \tag{2}$$

where x is the content of unsulfonated impurities in the test aromatic hydrocarbon in mole %; a is the weight of solvent in g; b is the aliquot of test aromatic hydrocarbon, in g; M is the molecular weight of the test aromatic hydrocarbon; M_1 is the molecular weight of the solvent; Δt is the depression of the crystallization temperature of the solvent caused by the presence of unsulfonated impurities left in it after removal of aromatic hydrocarbon by sulfuric acid; a is the depression in crystallization temperature of the solvent caused by 1 mole % of impurity.

Derivation of Equation (2) is not included because of lack of space.

Cyclohexane is recommended as the solvent for the cryoscopic method for quantitative determination of unsulfonated impurities in aromatic hydrocarbons. It is only for the analysis of benzene that cyclohexane cannot be used, since cyclohexane itself may form part of the unsulfonated impurity in benzene and cannot therefore be detected. In such a case cyclohexane can be substituted by another solvent, e.g. cyclohexylcyclohexane (dicyclohexyl).

The value of "a" for cyclohexane was assumed to be 2.42 as before [2].

When cyclohexane is used as solvent, Equation (2) may be transformed to give the following equation by substitution of the numerical values of "a" and M (2.42 and 84.17):

$$x = \frac{1 \cdot 19a \cdot M}{b(2.42 - \Delta t)} \qquad (3)$$

During analysis of individual aromatic hydrocarbons, the theoretical value of the molecular weight of the hydrocarbon is taken, since this value does not differ appreciably from the actual molecular weight of the mixture of aromatic hydrocarbon and a small amount of unsulfonated impurity. When aromatic hydrocarbons whose molecular weight is not known are being analyzed, e. g. hydrocarbons isolated from some cut or other, the molecular weight must be determined experimentally.

The accuracy of the cryoscopic method for quantitative determination of unsulfonated impurities in aromatic hydrocarbons also depends on the constancy of the value of "a" for cyclohexane. As is evident from the results given in [2] and in Table 3, the value of "a" for cyclohexane is, on the average, 2.42 for most test compounds; the deviations from this value are small. It is only in the case of a few compounds that this deviation becomes significant. Thus, on addition of methylcyclohexane to cyclohexane, the value of "a" for cyclohexane becomes 1.83, i. e. a value which is 24% lower than the accepted value of 2.42. Accordingly, when methylcyclohexane is present as an impurity in the aromatic hydrocarbons being tested, the amount of this impurity as found by the cryoscopic method in a cyclohexane will be 24% less than the true value.

The mean absolute accuracy for the cryoscopic method of determining impurities in the presence of a solvent is 0.1-0.2 mole %.

EXPERIMENTAL

The constants for the original hydrocarbons used are given in Table 1. The crystallization temperature was determined in a Beckmann apparatus used for determination of molecular weight; this apparatus was provided with an automatic stirrer and a normal thermometer with a scale covering −30 to +20° and having scale divisions of 0.1°. The mercury bulb of the thermometer was immersed in the test liquid. The temperature was read with an accuracy of hundredths of a degree by means of a lens. Alcohol kept at the required temperature with solid carbon dioxide was used as the coolant. The difference between the crystallization temperature of the test mixture and the temperature of the cooling bath should not exceed 1-2°.

TABLE 1

Physico-Chemical Properties of the Original Hydrocarbons

Hydrocarbons	$t°$ crystallization	$t°_{760}$	d_4^{20}	n_D^{20}	Unsulfonated residue content, in mole %
Cyclohexane	6.00	80.45— 80—65	0.7787	1.4260	—
Benzene	5.53	79.80	0.8790	1.5010	0.04
n-Heptane	—	—	0.6839	1.3878	—
Methylcyclohexane	—	—	0.7693	1.4230	—
Methylbenzene	95.2 0.2	110.8	0.8669	—	0.00
Ethylbenzene	—	—	0.8658	1.4945	0.1
Decahydronaphthalene	—	—	0.8710	1.4690	—
1-Methylnaphthalene	—	239.0— 241.0	—	1.6090	1.1
n-Hexadecane	17.2	—	—	1.4345	—

The unsulfonated impurities in aromatic hydrocarbons were determined as follows: 10-13 ml of cyclohexane with a known crystallization temperature was weighed on an analytical balance with an accuracy of

1 mg, and mixed with an approximately equal amount (in moles) of test aromatic hydrocarbon, weighed out to the same accuracy. The mixture was treated in a separating funnel whose capacity was about 80 ml with three times its volume of 98 ± 0.5% sulfuric acid for 30 minutes. During sulfuric acid treatment, the loss as a result of evaporation did not exceed 0.2%.

TABLE 2

Experimental Determination of the Value of "*a*" for Cyclohexane (depression of crystallization temperature by addition of 1 mole % of impurity)

Impurity added	Amount of impurity added, mole % N	Depression of crystallization temp. Δt, in °	Depression of crystallization temp. resulting from addition of 1% impurity, "*a*"
n-Heptane	3.99	9.78	2.45
n-Heptane	3.38	8.25	2.44
Methylcyclohexane	2.91	5.37	(1.84)[*]
Methylcyclohexane	3.45	6.30	(1.83)[*]
Toluene	4.74	10.85	2.29
Toluene	2.19	5.02	2.29
Ethylbenzene	3.56	8.58	2.41
Ethylbenzene	3.06	7.44	2.43
Decahydronaphthalene	2.99	7.50	2.50
Decahydronaphthalene	3.44	8.65	2.51
1-Methylnaphthalene	2.64	6.50	2.46
1-Methylnaphthalene	2.58	6.53	2.53
n-Hexadecane	1.48	3.66	2.47
n-Hexadecane	1.53	3.62	2.37
Mean value			2.43

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[*] These numbers were not taken into account during calculation of mean values

After separation of the phases, the acid was removed and the remaining hydrocarbon layer shaken again with an equal volume of fresh sulfuric acid of the same concentration. After removal of the acid, the crystallization temperature of the hydrocarbon layer was determined. Treatment of the hydrocarbon layer with fresh lots of sulfuric acid was continued until the crystallization temperature of the hydrocarbon layer did not change; usually, only one additional acid treatment was necessary. Additional crystallization and dehydration over calcium chloride of the cyclohexane solution do not change, as a rule, its crystallization temperature. Consequently, in the case of aromatic hydrocarbons with molecular weights below 150, it is possible, where it is necessary to speed up analysis, to omit neutralization and dehydration of the intermediate cyclohexane solutions, and only adopt additional neutralization and dehydration for controlling the correctness of the crystallization temperature of the final cyclohexane solution. On the basis of the experimental results obtained, the content of unsulfonated impurity was calculated by means of Equation (3).

The value of "*a*" for cyclohexane, i. e. the depression in crystallization temperature caused by addition of 1 mole % of impurity, was determined by adding 1.5 to 4 mole % of various hydrocarbons, and determining the depression in the crystallization temperature of the cyclohexane (Δt) caused by the impurity added artificially. The value of "*a*" was calculated by means of Equation (4).

$$a = \frac{\Delta t}{N} \qquad (4)$$

where N is the amount of impurity added in mole %.

TABLE 3.

Checking the Accuracy of the Volumetric Method for Quantitative Determination of Unsulfonated Impurities in Aromatic Hydrocarbons

Hydrocarbon	Unsulfonated impurity, % by volume		Deviation (actual content minus amount found)	
	Actual	Found	% Volume (absolute)	Relative, %
Benzene	3.5*	0.8	+2.7	77
Benzene	3.5*	1.0	+2.5	71
Toluene	1.2**	0.0	+1.2	100
Toluene	1.2**	0.0	+1.2	100

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* Composition of unsulfonated impurity: 1.2% volume cyclohexane, 2.0% volume n-heptane, and 0.3 mole % (taken as being equal to 0.3% volume) of unsulfonated impurity present in the original benzene.

** Cyclohexane was used as the unsulfonated impurity

TABLE 4

Accuracy of the Cryoscopic Method for Quantitative Determination of Unsulfonated Impurities in Aromatic Hydrocarbons When Cyclohexane is Used as Solvent

Composition of the impurity in mole %:

1) 0.99% of n-heptane, and 0.04% of the unsulfonated impurity present in the original benzene; 2) 1.45% of n-heptane, 1.23% of methylcyclohexane, and 0.04% of the unsulfonated impurity present in the original benzene; 3) n-Heptane (1.16%); 4) 0.86% decahydronaphthalene, and 1.09% of impurity contained in the original 1-methylnaphthalene; 5) 1.67% decahydronaphthalene, 0.66% n-hexadecane, and 1.67% of the unsulfonated impurity present in the original 1-methylnaphthalene.

Test aromatic hydrocarbon (AHC)	Actual content of unsulfonated impurity, in mole %	Content in test mixture, in g		Δt in °C	Content of unsulfonated impurity found, in mole %	Deviation (actual content minus content found)	
		AHC	Cyclohexane			Mole % (abs.)	Relative, %
Benzene	1.03^1	10.060	11.026	2.50	1.06	−0.03	−2.9
Benzene	1.03^1	11.692	9.859	3.30	1.08	−0.05	−4.9
Benzene	2.72^2	30.452	10.489	8.04	2.38	+0.34	+13
Benzene	2.72^2	10.379	10.394	5.88	2.32	+0.40	+15
Toluene	1.16^3	10.530	10.886	2.53	1.20	−0.04	−3.5
Toluene	1.16^3	10.340	10.314	2.65	1.21	−0.05	−4.3
1-Methylnaphthalene	1.95^4	7.873	11.270	1.55	1.56	+0.39	+20
1-Methylnaphthalene	1.95^4	12.041	10.027	3.05	1.80	+0.15	+7.7
1-Methylnaphthalene	3.34^5	11.902	9.202	6.20	3.43	−0.09	−2.7
	Mean deviation					0.16	7.5
	Maximum deviation					+0.39	+20

Results of determinations of "*a*" are given in Table 2.

The mean experimental value found for "*a*" of cyclohexane is 2.43; it practically coincides with the value of 2.42 calculated on the basis of the heat of crystallization of cyclohexane (639.3 calories/mole) and is taken as being the most reliable value in the present work. Without taking into account methylcyclohexane and toluene, the maximum deviation of the value found experimentally for "*a*", on addition of various hydrocarbons to cyclohexane, is 3%; only in the case of toluene was it found to be 6%. It is clear therefore that with individual exceptions (methylcyclohexane, toluene) the maximum possible error which may result from variations in the value of "*a*" for cyclohexane does not exceed 3% (relative).

The volumetric method [1] for quantitative determination of unsulfonated impurities was checked on two synthetic mixtures as follows.

Into the lower bulb of a buret used for sulfonation was introduced 50 ml of sulfuric acid containing 5% of free sulfur trioxide; this was followed by 25 ml of the dehydrated aromatic hydrocarbon in 4-5 lots (5-6 ml each) in the course of 15-20 minutes. The mixture was thoroughly agitated and cooled with water. After addition of all the test hydrocarbon into the sulfator, the mixture was thoroughly shaken for 15 minutes. The mixture was allowed to stand for 2 hours. The number of milliliters of unsulfonated product was multiplied by 4. The number obtained was expressed as a percentage content of unsulfonated impurity as percent volume.

Results obtained during checking of the volumetric method of determining unsulfonated impurities in aromatic hydrocarbons are given in Table 3.

As these results show the method gives results which are far too low. For a content of 1% of unsulfonated impurity, the volumetric method, in general, is incapable of detecting them. When 3.1% of unsulfonated impurity was present, the volumetric method found only 0.8% of the impurity, i. e. only a quarter of the amount actually present.

The cryoscopic method for the quantitative determination of unsulfonated impurities in aromatic hydrocarbons, using cyclohexane as solvent, was checked on synthetic mixtures of benzene, toluene, and 1-methylnaphthalene, with alkanes and cyclanes as unsulfonated impurities (Table 4).

The mean deviation between the amount of unsulfonated impurity actually found and the amount taken was found to be 0.16% (absolute). As was to be expected, an increased deviation (towards lower values) was observed when methylcyclohexane was present in the unsulfonated impurities. When these experiments are excluded, the mean deviation then becomes 0.10% (absolute).

SUMMARY

1. A cryoscopic method has been developed for the quantitative determination of unsulfonated impurities in aromatic hydrocarbons using cyclohexane as solvent. When this method is used, it is possible to carry out a quantitative determination of impurities in the form of alkanes and cyclanes (apart from cyclohexane) present in aromatic hydrocarbons, with an absolute accuracy of 0.1-0.2% (mole).

2. The cryoscopic method for quantitative determination of unsulfonated impurities may be used in those cases where the accuracy of the volumetric method is not enough, or when the volumetric method is, in general, inapplicable, as for example in the case of high molecular weight or crystalline aromatic hydrocarbons.

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* [See C.B. translation].

BRIEF COMMUNICATIONS

DETERMINATION OF THE ISOTOPIC COMPOSITION OF LEAD

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Determination of the isotopic composition of the lead from various minerals and rocks containing 10^{-2}-10^{-4}% of lead involves considerable difficulty resulting from the necessity of separating sufficient lead and the possibility of picking up lead from external sources during selection and preparation of test samples for analysis. A study of isotopic composition also becomes impossible in those cases where the mineral, although it contains much lead, is not available in sufficient amounts to yield 1 mg of lead, or at least not less than a few tenths of a milligram. In view of these facts it became necessary to develop a new technique by means of which it would be possible to determine the isotopic composition of lead when only small amounts are available.

In 1955 a group of American authors published a method [1] for determining the isotopic composition of lead in which the amount of metal required for analysis could be reduced to a few micrograms. The method of isotopic dilution was used for this purpose; thus, a few micrograms of the test lead was mixed with 25 μg of standard lead of known isotopic composition. For measurements the principles of surface ionization and electronic amplification were used.

Normally, the isotopic analysis of lead in amounts of the order of 1 mg have been carried out by us on a type MS-3 mass-spectrometer as follows. The lead was extracted from the sample and converted into its iodide; the latter was then introduced into an ion source. In the ion source the lower cathode was replaced by a tungsten band 1.5-2 mm wide; this was fixed directly in the ionization chamber. In order to get the lead iodide into the mass-spectrometer it is necessary to remove the ionic source, and to deposit a fine layer of the lead iodide on the tungsten band preliminarily moistened with twice distilled water. The lead iodide is firmly held on the tungsten band, both during the time it is being deposited on the band in the source and during the time the apparatus is being prepared for work. This method of introducing the sample enables one to use a gas source for analysis of the solid phase. The lead iodide introduced directly into the ionization chamber of the ion source was evaporated into it by passing a stabilized current through the tungsten band, and ionized with an electron beam; when this was done Pb^+ and PbI^+ ions were formed in approximately equal amounts, so that it was possible to measure masses of 204-208 and 331-335 in the spectra. In the spectra, masses of 204-208 were registered from the ratios of peaks with masses of 206, 207, and 208, i.e. the direct ratio of $\frac{Pb^{207}}{Pb^{206}}$ and $\frac{Pb^{208}}{Pb^{207}}$ by a compensation method. The collector slits were altered so that it was possible to register two neighbouring peaks simultaneously, and we were able to make a direct record of the ratio of the amount of isotopes. In the spectra for masses of 331-335, where no mercury peak was superimposed on the peaks with masses of 331 (Pb^{204} I^{127}), the ratio of peaks with masses 331 and 333 was measured, i.e. Pb^{204}(Pb^{206} and the intensity of peaks with masses 331, 333, 334, and 335). The resolving power of the mass spectrometer should not be less than 1:500. Measurements made in various mass spectra, in the absence of superposition of any other peaks on the lead peaks, should agree, so that it should be possible to control the correctness of recording of the isotopic composition.

After each determination the apparatus had to be carefully cleaned from any lead which had been introduced; this was done by prolonged heating (5-6 hours) of the apparatus tube, while the cathode and tungsten band were cleaned by passing a current twice that used for normal operation of the instrument.

In developing the new technique the same method of introducing the sample into the apparatus was used, while the method of comparing the peak intensities during registration of the mass spectra was also the same; the only difference was that the lead iodide was introduced into the apparatus together with a carrier. The use of a carrier meant that it was not only possible to introduce micro amounts of lead into the apparatus, but it was also possible to increase the time for which the lead was evaporated uniformly to a considerable extent; this strongly affects the accuracy of the method. Initially, the carrier chosen was silver iodide with which lead iodide is readily coprecipitated; such a mixture of iodides, however, introduces difficulties during mass spectral analysis. Silver iodide does not permit one to get a stable ion beam and sharply depresses its intensity. When small amounts of lead were separated by means of excess potassium iodide, and the latter used as a carrier, the K_2I^+ ions gave peaks with masses of 205, 206, 207, 208 and 209; this was checked several times using pure potassium iodide. These peaks were superimposed on lead peaks (206, 207, 208); consequently, lead was precipitated with hydrogen iodide, and cuprous iodide was chosen as a carrier.

Mineral and place found	Amount of lead precipitated with carrier	Isotopic composition of lead			
		Pb^{204}	Pb^{206}	Pb^{207}	Pb^{208}
Pitchblende•, Kareliya	1000	⩽0.02 ±15%	88.27 ±1%	9.89 ±1%	1.82 ±1%
Same	10	⩽0.02 ±30%	88.28 ±1%	9.84 ±1%	1.82 ±1%
	7-8	⩽0.02 ±30%	88.25 ±1%	9.87 ±1%	1.86 ±1%
'	5	⩽0.02 ±30%	88.21 ±1%	9.89 ±1%	1.88 ±1%
Galenite• Kareliya	1000	1.53 ±1.%	22.24 ±1%	22.52 ±1%	53.71 ±1%
Same	8	1.53 ±3%	22.31 ±1%	22.60 ±1%	53.56 ±1%
Monasite••, Kareliya	1000	0.08 ±10%	17.55 ±1%	2.90 ±1%	79.47 ±1%
Same	10	0.08 ±30%	17.52 ±1%	2.91 ±1%	79.49 ±1%
Zircon•••, Ukraine	12	0.49 ±10%	17.08 ±1%	8.59 ±1%	73.84 ±1%
Orthite••••, Kareliya	9	0.28 ±10%	22.29 ±1%	6.14 ±1%	71.29 ±1%

• Results obtained with pure lead iodide without carrier

•• Sample from K. K. Zhirov's collection

••• Sample from A. I. Tugarinov's collection

•••• Lead leached from Orthite from V. S. Lebedev's collection

Lead was extracted as the dithizonate from test mineral after decomposition of the latter, in order to carry out isotopic analysis; the lead dithizonate was decomposed with nitric acid (1 : 100). To the solution thus obtained, containing 5-10 μg of lead (determined photometrically), was added on a watchglass about 0.5 mg of cuprous iodide and 3-4 drops of concentrated hydriodic acid, and the whole evaporated to dryness. The mixture of Cu_2I_2 and PbI_2 was carefully collected and transferred onto the tungsten band as described above. Control tests carried out with a radioactive indicator (RaD) showed that the loss of lead incurred on transferring the mixture of iodides to the tungsten ribbon did not exceed 10-15%.

The vessel was checked several times for absence of lead. The reagents were purified and then checked for freedom from lead by means of a mass spectrometer.

When the carrier had been chosen, and it had been established that 5-10 μg of lead was sufficient for analysis by means of the mass spectrometer, comparative analyses were carried out on samples of known isotopic -

composition (see the Table). Errors in measurement amount to 30% when the content of a particular isotope is less than 0.1%; normally, however, the error does not exceed 1%. Ion currents were of the order of $10^{-11} - 10^{-12}$ amperes.

Thus the method which we have suggested for determining the isotopic composition of lead in small samples (of the order of 5-10 μg) by using a carrier enables one to carry out measurements on Soviet mass spectrometers type MS-2 and MS-3 without carrying out any essential modifications on the latter. This method enables one to extend the range of investigations on the lead method of studying geochemical and geochronological processes.

The authors wish to thank A. P. Vinogradov for his help during this work.

SUMMARY

A method for determination of the isotopic composition of lead in micro samples (5-10 μg) is suggested. Lead iodide, with cuprous iodide as carrier, is brought into an ion source in which lead iodide is evaporated and ionized by means of an electron beam. Measurements of isotopic composition are carried out in the mass spectra range 204-208 and 331-335. Using this method, it is possible to use type MS-2 and MS-3 mass spectrometers without having to make any essential modifications in these instruments.

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SEPARATION OF COPPER AND NICKEL BY MEANS OF ION-EXCHANGE CHROMATOGRAPHY

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The principle of the separation of copper and nickel by means of an alkali solution of glycerol and a cation-exchange resin can be stated as follows. The solution containing copper and nickel is passed through a column containing a cation-exchange resin in the H-form. The copper and nickel cations are thereupon absorbed by the resin; an alkali solution of glycerol is then passed through this column. Copper is eluted as the glycerate while nickel remains as the hydroxide.

The following cation-exchange resins were tried in the work described here: sulfocoal, KU-1, SBS, SDV-2, and SDV-3, which are widely used at present in analytical chemistry.

First of all we established that it was possible to carry out quantitative extraction of copper alone from the cation-exchange resins SDV-2 and SDV-3 by means of an alkali solution of glycerol (Table 1). Tests were carried out on a column 1.8 cm in diameter and 50 cm long; the amount of resin used was 15 g.

TABLE 1

Cation-exchange resin	Copper absorbed, in mg	Solution passed through, in ml		Copper extracted, in mg		Copper extracted by alkali solution of glycerol, in %
		By the alkali solution of glycerol	HCl	By the alkali solution of glycerol	HCl	
Sulfocoal	162.1	600	400	106.8	57.0	65.9
KV-1	162.1	600	400	142.0	20.0	87.6
SBS	162.1	600	400	144.0	19.0	88.8
SDV-2	162.1	225	250	162.1	0.0	100.0
SDV-3	162.1	225	250	162.1	0.0	100.0

On decreasing the concentration of NaOH and glycerol it is necessary to increase the solution required for extracting the copper. On eluting the cation-exchange resins sulfocoal, KU-1, and SBS with the alkali solution, materials are eluted which color the filtrate yellow and complicate subsequent determination of copper. Only the cation-exchange resins SDV-2 and SDV-3 can be used for separating copper and nickel by means of an alkali solution of glycerol.

To separate copper and nickel, the test solution is passed through a column containing 15 g of either SDV-2 or SDV-3 in the H-form, at the rate of 1 drop per second. The cation-exchange resin is washed with 50 ml of water, and then with a solution containing 5 g of sodium hydroxide and 5 ml glycerol in 100 ml, until the filtrate gives a negative reaction for copper when tested with $K_4Fe(CN)_6$. The filtrate, which contains copper glycerate, is transferred to a 500 ml standard flask and made up to the mark with distilled water; 50 ml of this solution is taken for iodometric determination of copper. After elution of the copper, the cation-exchange resin is washed with distilled water until the filtrate only gives a weak alkaline reaction to phenolphthalein; next, a 5% solution of hydrochloric acid is passed through the resin until the nickel has been completely extracted (reaction with dimethylglyxome). The hydrochloric solution containing the nickel is transferred to a 250 ml standard flask and made up to the mark with distilled water; 50 ml of this solution is taken for determination of nickel by the dimethylglyoxime method. When the nickel content of the original solution is low, the hydrochloric acid solution is evaporated to dryness; the dry residue is dissolved in water and nickel then determined in this solution.

Results of separation of copper and nickel by means of an alkali solution of glycerol, using the cation-exchange resins SDV-2 and SDV-3 are given in Table 2.

TABLE 2

Taken, in mg		Solutions passed through column, in ml		Copper extracted, in mg		Nickel extracted in mg		Extracted, in %	
Cu	Ni	Alkali solution of glycerol	HCl	By the alkali solution of glycerol	HCl	By the alkali solution of glycerol	HCl	Cu by alkali solution of glycerol	Ni by HCl
62.1	184.5	500	225	146.2	16.2	0.0	184.5	90.20	100.0
196.5	107.4	300	225	187.5	9.5	0.0	107.5	95.42	100.0
196.5	80.5	300	200	188.0	8.5	0.0	79.9	95.68	99.25
196.5	53.7	300	200	190.5	6.5	0.0	53.4	96.94	99.44
196.5	42.9	300	200	196.5	traces	0.0	42.8	100.0	99.76
196.5	40.2	300	200	196.5	0.0	0.0	40.2	100.0	100.0
196.5	37.6	300	200	196.5	0.0	0.0	37.6	100.0	100.0
196.5	26.8	300	200	196.5	0.0	0.0	26.8	100.0	100.0
196.5	10.7	300	150	196.5	0.0	0.0	10.6	100.0	99.07
196.5	5.4	300	150	196.5	0.0	0.0	5.4	100.0	100.0
196.5	2.7	250	150	196.5	0.0	0.0	2.7	100.0	100.0
98.2	53.7	300	200	97.5	0.8	0.0	54.0	99.28	100.0
98.2	42.9	300	200	98.2	traces	0.0	42.9	100.0	100.0
98.2	40.2	300	200	98.2	0.0	0.0	40.2	100.0	100.0
98.2	37.6	300	200	98.2	0.0	0.0	37.6	100.0	100.0
49.1	53.7	300	200	48.8	0.3	0.0	53.7	99.40	100.0
49.1	42.9	300	200	49.1	traces	0.0	42.9	100.0	100.0
49.1	40.2	300	200	49.1	0.0	0.0	40.2	100.0	100.0

These results show that copper and nickel are quantitatively separated by an alkali solution of glycerol on SDV-2 and SDV-3. This technique of separating copper and nickel by means of SDV-2 and SDV-3 can be successfully used in analytical laboratories. The method has a number of advantages over known methods of separating copper and nickel. For a column 50 cm long, with a diameter of 1.8 cm and containing 15 g of the resin, the nickel content of the original solution should not exceed 40 mg. When the original solution contains larger amounts of nickel, extraction of copper from the resin by the alkali solution of glycerol is complicated, and some of the copper remains on the column together with the nickel. Thus, when the original solution contained 107.4 mg Ni and 196.5 mg Cu, 4.58% of the copper remained on the column with the nickel, while for a solution containing 42.9 mg of Ni, only traces of copper remained on the resin.

Incomplete extraction of copper from the cation-exchange resin during separation of mixtures containing more than 40 mg of nickel is, presumably, the result of coprecipitation of copper with nickel hydroxide.

SUMMARY

A study has been made of the possibility of separating copper and nickel by means of an alkali solution of glycerol on the cation-exchange resins: sulfocoal, KU-1, SBS, SDV-2, and SDV-3. It was found that of these resins, only SDV-2 and SDV-3 are capable of ensuring quantitative separation of copper and nickel.

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THE SYSTEM MnO_4^- – Br^- UNDER THE CONDITIONS USED FOR POLAROGRAPHIC DIFFERENTIAL TITRATION

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Methods for selective determination of the elements are of great interest for chemical analysis. Special difficulties are encountered during determination of small amounts of manganese in objects which contain chromium, vanadium, cobalt, and other elements when use is made of oxidation-reduction reactions. A considerable amount of work has been devoted to determination of manganese in the presence of the metals indicated, and various methods have been suggested for achieving a practical solution to this problem [1-8]. When the manganese content is comparatively low, most of it is converted into the permanganate ion. When the latter is titrated, it is desirable to choose a reducing agent which will reduce the MnO_4^- ion quantitatively, but at the same time will not react with the other oxidizing agents (dichromate, vanadate ions, etc). With this idea in mind such reducing agents as $(VO)SO_4$ [9, 10] and $Hg_2(NO_3)_2$ [11] have been proposed. Potassium bromide is of great interest as a reducing agent in view of the value of its normal oxidation-reduction potential [12], and also because it is possible in this case to use polarographic differential titration [13]. When potassium bromide is used for determination of the permanganate ions, three methods are possible: 1) direct titration with bromide solution; 2) determination of the amount of bromine liberated during interaction of bromide and permanganate ions; and 3) determination of standard potassium bromide solution which has not reacted with permanganate.

The principle of polarographic differential titration can be briefly described as follows. During polarization of two similar metal electrodes by a very small constant current (about 2 microamps), a constant e.m.f. is set up which leads to a corresponding slope of the polarographic curve with respect to the straight line of the zero current. At the equivalence point there is a sharp change in the e.m.f. The deciding factor in polarographic titration is the polarization or depolarization of one of the electrodes. We have studied the behavior of the system MnO_4^- – Br^- under conditions used for polarographic differential titration.

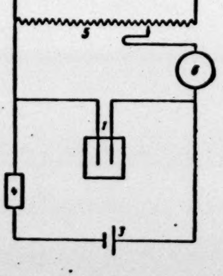

Fig. 1. Setup of the apparatus used for differential polarographic titration.

The apparatus used is shown schematically in Fig. 1. The electric circuit consists of two similar platinum electrodes 1 (wire 20 mm long and 0.5 mm diameter), a 45-40 volt battery 3, an auxiliary battery 2 with a voltage of 2.5-5.0 volts, resistance 4 of 22 megohms, a high ohm potentiometer 5, direct current type PPTV-1, and an electro-magnetic mirror galvanometer 6 type 21/5. 0.002--0.02 M solutions of $KMnO_4$ and 0.01-0.1 M KBr were prepared. The volume of the solution being titrated was 21 ml, the applied voltage was 35 volts; the auxiliary accumulator had a voltage of 2.5 volts. A 2 ml microburet with scale divisions of 0.01 ml was used. The solutions were stirred with an electric stirrer (200-300 revolutions/minute).

Effect of Hydrogen Ion Concentration and Nature of the Acid Anion. Permanganate ions react with bromine ions in acid solution as follows [14]:

$$2MnO_4^- + 10Br^- + 16H^+ = 2Mn^{2+} + 5Br_2 + 8H_2O$$

Our experiments showed that the reaction only follows this course when a considerable excess of bromide ions is introduced. When permanganate ions are titrated directly with potassium bromide in acid solution, the permanganate is mainly reduced to tri- and quadrivalent manganese. The extent to which permanganate ions are reduced depends not only on hydrogen ion concentration, but also on the nature of the acid anion. Sulfuric acid is the most suitable. In the presence of this acid, MnO_4^- ions are mainly reduced to Mn^{3+}. The reaction rate and the value of the polarization jump at the equivalence point increase with increasing acidity. The minimum acidity depends on the manganese content. Thus, during titration of 0.0001 M MnO_4^- solution, the minimum H_2SO_4 concentration at which the reaction proceeds quantitatively, though very slowly, is about 2 g equivalents/liter, while for a 0.001 M MnO_4^- solution, the H_2SO_4 concentration is about 1.5 g equivalents/liter. Best results are obtained in the presence of 3 N H_2SO_4 (Fig. 2, Curve 1).

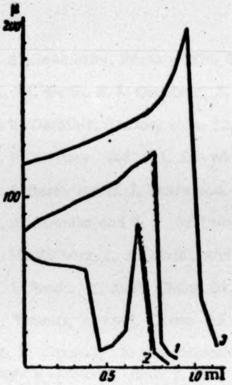

Fig. 2. Polarization curves for titration of Mn^{VII} with potassium bromide. Titration curves: 1) 1 ml of 0.02 M $KMnO_4$ solution + 20 ml of 3 N H_2SO_4 (titration was carried out with 0.1 M KBr at a temperature of 18°); 2) 1 ml of 0.02 M $KMnO_4$ + 20 ml of 2 N H_2SO_4 (titration carried out with 0.1 M KBr solution at a temperature of 40-60°); 3) concentration of 0.002 M Mn.

Effect of Phosphoric and Nitric Acids. Many materials dissolve in nitric and phosphoric acids. We established that orthophosphoric acid does not interfere with titration as long as its concentration does not exceed 0.05 N. Nevertheless, at concentrations of 0.5-0.6 N H_3PO_4 and 2 N H_2SO_4, reduction of MnO_4^- proceeds to Mn^{IV} and not to Mn^{3+}. Nitric acid also favors reduction of the greater part of MnO_4^- ions to Mn^{IV} and not to Mn^{3+}. Thus, the presence of appreciable amounts of nitric acid, and particularly of phosphoric acid, leads to a non-stoichiometric reaction.

Effect of Temperature. At elevated temperatures (of the order of 40-60°) reduction of MnO_4^- proceeds to a significant extent to Mn^{2+}; the reduction is not quantitative; the value of the jump in the polarization current at the equivalence point is depressed. Furthermore, in 2 and 3 N H_2SO_4, the polarization curve has a minimum and a maximum, probably as a result of the gradual multistage reduction of MnO_4^- ions (Fig. 2, Curve 2). At higher H_2SO_4 concentrations (4-6 N) the polarization curve has the normal shape. The solution was heated during titration by means of specially constructed apparatus.

Effect of Complex Formation. In order to ensure quantitative reduction of MnO_4^- to Mn^{3+}, and to increase the reaction rate, we made use of complex formation between Mn^{3+} and fluoride and pyrophosphate ions (in the form of NH_4F and $Na_4P_2O_7$ respectively). In the presence of $P_2O_7^{4-}$ and F^- ions the permanganate ion is quantitatively reduced to Mn^{3+}; the reaction rate, however, is still slow, particularly in the presence of $Na_4P_2O_7$, since in this case the acidity of the solution is lowered.

Effect of the Ions. $Cr_2O_7^{2-}$, VO_3^-, Co^{2+}, WO_4^{2-}, MoO_4^{2-}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+}. When the ions listed are present in solution, they do not interfere with the reaction between MnO_4^- and Br^-; nevertheless, Fe^{3+} interferes with establishement of the potential of the electrodes. In the presence of silver ions a precipitate of AgBr is formed, but when all the silver ions have been precipitated, reaction between bromide and permanganate ions starts; at the point where precipitation of silver ions is complete no jump is observed on the polarization curve; subsequently, however, the shape of the curve is normal.

Effect of Excess Ammonium Persulfate. Excess ammonium persulfate, corresponding to a concentration of 0.1 M in solution, does not affect titration results, but slows down the rate at which the electrode potential is established. During selective determination of comparatively small amounts of manganese in steels (Mn concentration of 0.0002 N) by the method described (Fig. 2, Curve 3) there should be no excess of phosphoric or nitric acids present; titration should be carried out fairly slowly, particularly near the equivalence point, in order to get normal polarization curves.

SUMMARY

The behavior of the system $MnO_4^- - Br^-$ has been studied under the conditions used in polarographic differential titration. The optimum concentration of sulfuric acid necessary to give a clearly defined polarization curve has been determined. The effect of various components which may be present in solution on the character of the polarization curve, and on reaction rate, has been studied. It has been established that it is possible to carry out selective determination of small amounts of manganese in samples of complex composition. The titration proceeds rather slowly.

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* [See C.B. translation.]

DETECTION OF COBALT

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Goldberg [1] detected cobalt with thiourea on the basis of the development of a color. On triturating solid materials containing cobalt with crystals of thiourea, or on heating dry thiourea with a few drops of cobalt solution, a dark blue, light blue, or green color, which rapidly disappears on addition of water, develops. Somewhat earlier [2], Isakov showed that on triturating cobalt salts with crystalline thiosulfate, a blue color also appears in this case which disappears on addition of drops of water. In our experiments, during trituration of cobalt sulfate or nitrate in a mortar with some thiosulfate crystals, a dark blue or blue color appeared. On moistening a few crystals of thiosulfate with one drop of solution, a blue color appeared when cobalt was present, the intensity of this color varied with cobalt concentration; there was no need to heat in this instance. The limit of identification was 2.0-2.5 μg Co. On addition of a few drops of water to the mixture obtained, the color disappeared rapidly. The color did not appear also on moistening the thiosulfate crystals with a relatively large amount of cobalt solution (1-2 ml).

Tests showed that the ions of the first and second groups, as well as ions Al^{3+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, Cd^{2+}, Ag^{+}, Pb^{2+} in amounts which are 1000 times that of the cobalt do not interfere with the detection of the latter, since they either do not react with thiosulfate, or form colorless compounds with it. Cu^{2+} ions are reduced by thiosulfate to colorless Cu^{+} ions, and, thanks to this, copper also does not interfere with cobalt detection. The sensitivity of the reaction in the presence of large amounts of the ions listed is equal to 3.0 μg of Co. Nickel ions in amounts which are six times that of cobalt interfere with the determination as a result of the characteristic color. Chromium ions also interfere.

On carrying out the reaction by a drop technique – by moistening crystals of thiosulfate with a drop of test solution – Hg_2^{2+} ions are reduced to free mercury whose black color masks the blue color. Solutions which contain bismuth color thiosulfate crystals yellow to start with; the color then changes to brown, while the final color is black. Tin and antimony also interfered, since they give bright yellow or orange colors.

In trying to explain the reason for the development of a blue color on triturating cobalt salts with thiosulfate, Isakov referred to the possibility of the formation of a compound $Na_2[Co(S_2O_3)_2]$ [2].

The development of a color when thiourea is used has been given a similar explanation.

Without touching here on the question of the possibility of the formation of colored complexes of cobalt with thiourea or thiosulfate, we wish to draw attention to the following important fact.

On adding 1-2 drops of water to a mixture of cobalt with thiosulfate or with thiourea, the color disappears comparatively rapidly, and the solution acquires the usual rose color of solutions of hydrated cobalt ions. This leads one to suggest that the blue color which develops is primarily the result of the breakdown of the hydrated shell and absorption of the water by thiosulfate, thiourea, and other compounds to which the drop of cobalt solution is added. It is known that anhydrous cobalt salts are blue in color. On evaporating such solutions, or on adding compounds which absorb water, the rose color of the solution changes over to blue as a result of dehydration [3].

$$[Co(H_2O)_6 Cl_2 \rightarrow [Co(H_2O)_n Cl_2] + (6-n) H_2O,$$

where $n < 6$, while on heating n becomes equal to zero [3].

The following experiments confirm what has been said:

1. The blue color appears on evaporating and carefully calcining a few drops of cobalt nitrate or sulfate in a porcelain basin. On adding 2-3 drops of water the blue color disappears immediately. It is characteristic that during interaction with thiourea the color only appears after heating, i. e. after removal of water, and is again destroyed on adding water.

2. Goldberg recommended that in order to detect cobalt in solution aqueous solutions of cobalt and thiourea should be mixed and then heated; after this a strip of filter paper should be immersed in the mixture and the filter paper then dried over a hot plate or burner. Our tests showed however that a similar color appears when a strip of filter paper is treated with a solution of cobalt on its own, i. e. in the absence of thiourea, and this paper then carefully dried as before.

3. A blue color is obtained on moistening calcined calcium chloride with a drop of cobalt solution, or when dry cobalt salts are triturated with this salt, or cobalt is added to other dehydrating materials – phosphorus pentoxide, concentrated hydrochloric acid, and anhydrous sulfuric acid.

We would like to suggest therefore that the appearance of a blue color during interaction of cobalt with thiosulfate, thiourea, etc, is not related to formation of complex compounds, but is the result of the dehydration of the aquo-complexes of cobalt by thiourea, thiosulfate, and other dehydrating compounds.

SUMMARY

Some ideas are outlined regarding the reasons for the development of a blue color during detection of cobalt by means of thiosulfate, thiourea, and other compounds. It has been shown that it is possible to detect cobalt in dry salts and in solution by triturating the powders, or by moistening not only with thiosulfate and thiourea but also with other dehydrating agents, and even by careful drying of a filter paper moistened with a cobalt solution. In all cases the blue color develops as the result of the dehydration of aquo-complexes of cobalt.

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* [See C.B. translation.]

AMPEROMETRIC TITRATION OF AMMONIUM SULFATE IN MEDICINAL SERUMS

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$(NH_4)_2SO_4$ can be determined in medicinal serums by adding excess standard $Pb(NO_3)_2$ solution which is back titrated with a solution of $K_4Fe(CN)_6$ using an anodically polarized rotating platinum electrode [1].

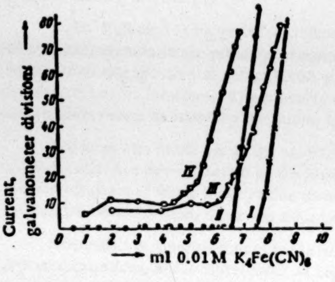

Fig. 1, Titration curves:
I) $Pb(NO_3)_2$ solution; II) excess $Pb(NO_3)_2$ in water after precipitation of $(NH_4)_2SO_4$; III) – IV) excess $Pb(NO_3)_2$ after precipitation of $(NH_4)_2SO_4$ in the serum.

A known volume of the serum is placed in a 200 ml standard flask and 20 ml of about 0.05 M $Pb(NO_3)_2$ solution added; the flask is immersed for 3-5 minutes in boiling water; after cooling, about 66 ml of acetone (or ethanol) is added and the volume made up to the mark (200 ml) with water. An aliquot (30 ml) is transferred to the titration vessel and 0.2 ml of a saturated solution of KNO_3 added; excess $Pb(NO_3)_2$ is then titrated with 0.01 M $K_4Fe(CN)_6$. Titration curves are shown in Fig. 1.

The equivalence point is found by extrapolating the upper, ascending section of the titration curve to intersect the abscissa. The empirical titer of the $Pb(NO_3)_2$ solution is determined under similar conditions. The method gives satisfactory results during determination of about 0.1% of $(NH_4)_2SO_4$ in serums.

SUMMARY

$(NH_4)_2SO_4$ is determined in medicinal serums by adding excess $Pb(NO_3)_2$ solution and back titrating with $K_4Fe(CN)_6$.

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QUALITATIVE AND SEMI-QUANTITATIVE DETERMINATION OF FLUORIDE BY A SPOT METHOD

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The following reactions have been used for detecting fluoride in analytical practice: microcrystalloscopic reactions based on the formation of $Ba[SiF_6]$ and $Na_2[SiF_6]$ [1], reactions based on precipitation of the fluorides of calcium, barium, and lanthanum [2], decolorization of zirconium-alizarin lakes [1, 3] and ferric thiocyanate [1], and etching of glass [1].

L. M. Kulberg has suggested a method of detecting fluoride [4] based on the deepening of the blue color of iron ferrocyanide in the presence of excess thiocyanate ion under the action of fluoride ions. It is possible by means of this reaction to detect 0.033 γ F at a limiting dilution of 1 : 50,000. Borates, silicates, oxalate, and ferricyanides interfere. The intensity of the color depends on the acidity of the solution. The need for excess thiocyanate as stated by the author has not been substantiated.

We have also made use of the reaction between ferric ferrocyanide and fluoride ions for the detection and semi-quantitative determination of the latter; we used a spot technique on filter paper. We found that the blue colored solutions of ferric ferrocyanide changed to a light violet in the presence of fluoride ions,' and, depending on fluoride concentration, there was a further change to a lilac color.

The effect of fluoride ions is not specific. Phosphates, oxalates, and tartrates give a cornflower blue at low concentrations, and a violet color at higher concentrations. The presence of excess thiocyanate is not only not essential, but is even undesirable, since the reaction sensitivity in the absence of thiocyanate is twice that in its presence.

Fluoride concentration mg/ml	Fluoride concentration found, mg/ml	Absolute error, in mg/ml	Relative errror, in %
0.40	0.40	—	—
1.00	1.00	—	—
1.15	1.10	0.05	−4.8
1.68	1.70	0.02	+1.1
1.68	1.60	0.08	−4.8
1.70	1.80	0.10	+5.8
1.75	1.80	0.05	+2.8
2.00	2.30	0.30	+15.0
2.00	2.00	—	—
2.85	2.80	0.05	−1.7
3.00	3.20	0.20	+6.7
3.50	3.50	—	—
4.00	4.40	0.40	+10.0
4.40	4.30	0.10	−2.2
9.00	8.70	0.30	−3.3

When ferric chloride solution is added to an equimolar mixture of potassium ferrocyanide and ammonium fluoride, the red-violet color which first appears changes to a rose color, and then to blue, depending on the amount of ferric chloride. The change in color is determined by the formation of a colored compound.

The violet compound formed, which is stable enough, can be used for detecting fluorides.

We have worked out the following techniques for detecting fluoride ions.

1. When the fluoride concentration is fairly high (greater than 1 mg/ml). A drop of 0.1 M potassium ferrocyanide is placed on a filter paper and allowed to soak in; a drop of test solution is then added. A drop of 0.1 M ferric chloride is next placed on the same spot. A blue spot of ferric ferrocyanide is immediately formed, and when fluoride is present this spot is bordered by a rose or lilac

colored ring, according to the fluoride concentration. Using this method it is possible to detect 2-3 γ of F in a drop (0.005 ml).

2. When the fluoride content is less than 0.4 mg/ml the order in which the reagents are added is changed since the lilac ring is poorly defined. In such cases a blank has to be carried out. Two drops of 0.005 M ferric chloride are placed at a small distance from each other on a filter paper on which ferrocyanide has been placed beforehand. Two greenish-blue spots are thereby obtained; on one of them is placed a drop of test solution. When fluoride ions are present the color changes to violet or lilac. The colors obtained in both cases are then compared.

It is possible to detect 0.01 γ of F at a limiting dilution of 1:100,000 when using this method.

Anions which interfere with this reaction (phosphates, borates, silicates, tartrates, and oxalates) are precipitated by means of silver nitrate on a watch glass or in a cavity on a spot plate. Excess silver ions are precipitated by addition of a few crystals of sodium chloride. The solution is filtered through a filter paper by means of a capillary.

Fluoride ions are detected in acid media. Large amounts of sulfate, nitrate, nitrite, chloride, and bromide do not interfere.

Formation of the colored compound of fluoride and ferric ferrocyanide can be used for a rapid semi-quantitative determination of fluoride.

Standard solutions with a known fluoride content are prepared for carrying out semi-quantitative determinations.

Several drops of potassium ferrocyanide solution are placed on different places on a filter paper, drops of ferric chloride solution are then superimposed on top of these spots. Blue green spots are obtained. A drop of test solution is placed on one of these spots, while drops of the various standard solutions prepared are placed on the remaining spots. Fluoride content can then be determined by comparison of the colors. Next, two more spots of ferric ferrocyanide are prepared alongside each other; a drop of test solution is applied to one spot, and a drop of standard solution whose fluoride concentration is the nearest to that of the test solution placed on the other. The concentration of the test solution is determined by comparison, the spots while still moist being examined on the filter paper in transmitted light. Results of semi-quantitative determination of fluoride are given in the Table.

0.01 ml of test solution is sufficient. A determination can be carried out in one or two minutes.

The errors do not exceed the tolerance limits set by the Ministry of Geology for quantitative determination of fluoride in mineral raw materials [5].

SUMMARY

A spot technique has been developed for detection of fluoride ions; it is based on formation of a colored compound of fluoride with ferric ferrocyanide. The reaction is fairly sensitive and enables one to detect 0.01 γ of F at a limiting dilution of 1:100,000. A method is described for the rapid semi-quantitative determination of 0.5 to 10 mg/ml of F.

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DETECTION OF NICKEL IN THE PRESENCE OF COBALT, COPPER, AND OTHER ELEMENTS

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Eight-nine drops of test solution are placed in a test tube and 7-8 times this quantity of an aqueous solution of ammonium carbonate, saturated with the latter, added at room temperature; this is followed by 0.5 ml * of a suspension of dimethylglyoxime in carbon tetrachloride,** and the whole shaken vigorously.

When nickel is present the lower carbon tetrachloride layer acquires the red color characteristic for nickel, while a precipitate of the same color subsequently appears.

Detection of nickel is possible at a ratio of Ni : Co : Cu = 1 : 500 : 1000. The limit of identification is 1.8 μg of nickel. The limiting dilution is 1 : 200,000. The optimum solution pH is 8-9.

SUMMARY

A method has been developed for fractional detection of nickel in the presence of large amounts of cobalt, copper, and other elements, by means of dimethylglyoxime.

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* When the nickel content is low, a large amount of suspension complicates detection of nickel.

** The suspension is prepared by vigorously shaking 2 g of dimethylglyoxime with 30 ml of carbon tetrachloride.

CHRONICLE

QUESTIONS RELATING TO ANALYTICAL CHEMISTRY DEALT WITH AT THE ALL-UNION SCIENTIFIC TECHNICAL CONFERENCE ON THE USE OF RADIOACTIVE AND STABLE ISOTOPES AND RADIATION IN SOCIAL ECONOMY AND SCIENCE.

(Moscow 4 - 12 April, 1957)

The conference was convened by the USSR Academy of Sciences and the Chief Administration on the Use of Atomic Energy of the USSR Soviet of Ministers.

The use of radioactive and stable isotopes for solving theoretical and practical questions in analytical chemistry was considered at meetings of the sections on analytical chemistry and control of production, and partly at meetings of the section on radiochemistry. A lot of attention was devoted to all the basic fields of application of radioisotopes in analytical chemistry: their use during development of general problems, and the practical application of such methods of modern analytical chemistry as precipitation and coprecipitation, chromatographic separation, extraction, spectrographic analysis, etc.; their use during development and improvement of new methods of analysis based on the measurement of the intensity of radiations (radioactivation analysis, isotope dilution, radiometric titration); and, finally, for solving purely applied problems connected with the analysis of individual materials. Twelve reports were heard in all on these questions.

A report delivered by G. I. Gorshtein and G. V. Abramova (Institute of Chemical Reagents and the "Red Chemist" factory) dealt with theoretical problems of purifying materials by crystallization and precipitation, and gave examples of how to prepare inorganic materials in a high state of purity by using radioactive indicators. The authors gave results on the purification of reagents from non-isomorphous and isomorphous impurities. In the case of non-isomorphous impurities, the concentration of the main component in the mother liquor is of prime importance; a low solubility for the salt of the macro component favors purification from impurities to a considerable extent. The correctness of the linear law of the distribution of isomorphous micro-components (Khlopin's law) has been confirmed experimentally for new types of aqueous-salt systems. Furthermore, it was established that the value of the distribution coefficient remains constant in many cases, on going from micro concentrations to a fairly wide range of macro concentrations of salt systems.

The important effect shown by the properties of the macro component on the nature of the distribution of the micro component was also pointed out by V. I. Grebenshchikova (RIAN) who participated in the discussion. V. R. Klokman (RIAN) gave results obtained during a study of the behavior of small amounts of material during distribution between a melt and a solid phase. M. S. Merkulova (Moscow State University) spoke about a study of the mechanism of the entry of ions of divalent metals into the lattice of salts crystallizing in the sodium chloride type of lattice. I. G. Shafran (Institute of Chemical Reagents) gave an address on "The Use of Labeled Atoms for Developing Chemical Methods of Analysis for Impurities in Reagents of a High Degree of Purity".

M. M. Senyavin (GEOKhI) gave a report on the importance and the scope of application of radioactive isotopes in chromatography. Radioactive isotopes make it possible to explain a number of theoretical questions in chromatographic separation (the relation between the amount of sorbed material and its concentration, etc.) and make it considerably easier to follow the path taken by a chromatographic process. The same report contained results of studies on the isolation of pure cesium, separation of sodium and potassium, and determination of yttrium in rare earth mixtures. In the latter instance use was made of a special combination of ion-exchange separation and the isotope dilution method.

A. K. Lavrukhina and F. I. Pavlotska's report (GEOKhI) contained results of work on chromatographic separation of promethium from uranium fission products. I. A. Korshunov (Gorky State University) spoke about chromatographic separation of radio-iron from radio-cobalt. At the radiochemistry session, P. V. Zimakov, A. G. Bykov, and I. A. Usacheva (Ministry of Chemical Industry) delivered a report on a new method of analyzing certain solutions containing uranium fission products. In this method, use is made of the capacity of charged ions to move under the influence of an electric current along a strip of paper moistened with electrolyte; the authors call this method the radioelectrochromatographic method.

Extraction methods play a very important part in practical analytical and radio chemistry. V. M. Vdovenko (RIAN) gave a review of extraction processes and their significance in the preparation and purification of radioactive isotopes. Vdovenko emphasized the importance of the theoretical aspects of extraction (the mechanism of extraction, choice of conditions, efficiency of the salting out effect, etc), and also gave a general property of a number of techniques commonly used – masking of other ions, re-extraction, use of the various valencies of the same element, etc. A. V. Nikolaev and N. M. Sinitsin reported on the characteristics of the behavior of ruthenium during extraction with tributylphosphate.

The use of labeled atoms has led to the solution of a number of important problems in spectrographic analysis. One of the fundamental problems in spectrographic analysis is the study of the effect of a number of factors (bulk composition, third components, etc) on the process of evaporation of elements from test elements and excitation of the atoms in the arc plasma. The use of radioactive indicators, as shown in the report read by E. E. Vainshtein (GEOKhI), has made it possible to study independently the path followed by these processes, and, on this basis, choose conditions for carrying out analysis which will ensure that the results obtained will be of the highest possible accuracy. The use of radioactive isotopes is also of great importance in developing spectrographic methods of analyzing materials of a high degree of purity; in this report results were included on the extent to which impurities had been removed during physical enrichment, using evaporation and subsequent condensation of impurities on a cooled electrode. Considerable attention was given in the report to a spectrographic method developed in the USSR for determination of uranium by means of U^{235} which was added to the sample, whereby it was possible to increase accuracy of determination to 1-2%.

A number of reports which were devoted to new methods for the quantitative determination of elements which are based on measurement of the intensity of radiation from radioactive isotopes, were also discussed. The reports of I. P. Alimarin and Yu. V. Yakovlev (GEOKhI) and of O.E. Zvyagintsev and A. I. Kulak (The D. I. Mendeleev Chemicotechnological Institute) were devoted to one of the most sensitive methods of analytical chemistry – radioactivation analysis – whereby it is possible to determine 66 elements in amounts ranging from 10^{-5}-10^{-12} g. The first report, which was really a review, was devoted to a description of the principles and advantages of the method, while a detailed description was also included of the work carried out by the authors on determination of Cu, Sb, and As, and the rare earths at contents of 10^{-7}% in metallic bismuth. The second report was devoted to results of the analysis of refined silver and cathodic nickel for their contents of Au, Pt, Pd, and Ir, to the determination of Cu, As, Te, Ni, and Co in antimony of a high degree of purity, and of Co, Cu, Te, As, and Sb in gold. The contents of the elements which were determined varied from 5×10^{-3} to 5×10^{-8} %.

A. Kh. Breger (The Karpov Physicochemical Institute), who participated in the discussion, gave results of the radioactivation determination of oxygen in metals on the basis of (γ, n) reactions which was carried out on a betatron. The sensitivity of the method can be increased to 0.01%.

I. E. Zimakov (State Institute of Non-Ferrous Metals) spoke in the discussion about a new variant of the method of isotopic dilution, whereby it is possible to avoid determination of the specific activity of the preparations separated, and to increase the sensitivity of the method to 10^{-6}-10^{-7}%.

The report of I. M. Gibalo (Moscow State University) and I. A. Sirotina (GEOKhI) which dealt with radiometric titration contained descriptions of new methods of determining Be and Zr by titration with phosphate containing P^{32}, and determination of Tl by titration with iodide, chromate, and phosphotungstic acid, or sodium tetraphenyl boron, using Tl^{204}. Non-aqueous solvents can be used for radiometric titration as V. S. Chernyi (Kharkov State University) pointed out in the discussion.

V. B. Gaidadymov (GEOKhI) pointed out the possibilities of reflection of β-particles as a method, taking as examples analysis of mixtures of Nb and Ta, Zr and Hf, Mo and W, and also determination of Pb in glass.

Some reports were devoted to the use of radioactive indicators for solving problems in applied analytical chemistry.

The use of labeled atoms for developing new methods and checking old methods of separating and determining elements was dealt with in the report of M. L. Troitskaya, E. N. Artemova, and A. M. Zaraisky (Institute of Non-Ferrous Metals). The work carried out by the authors on the completeness of separation of microgram amounts of a number of elements by various methods made it possible to develop fairly rapid methods for determining zinc in nickel, cobalt and cadmium, and to introduce corrections to the method used previously for determination of arsenic and phosphorus in nickel, and of copper, and indium in metallurgical dusts from lead and zinc production.

E. N. Nanobashvili (Georgian SSR Institute of Chemistry) spoke about the use of S^{35} for quantitative determination of a number of elements by precipitation as the sulfides. S. L. Tarabaev (Kazakh Academy of Sciences) dealt with determination of bound water in some crystallohydrates by means of labeled atoms.

The conference showed that radioactive isotopes are being widely and successfully used in the Soviet Union for solving theoretical and practical problems in analytical chemistry.

Yu. A. Zolotov and Yu. V. Yakovlev

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THE DEVELOPMENT OF RESEARCH ON ANALYTICAL CHEMISTRY IN THE USSR

A. P. Vinogradov

During the forty years following the Great October Socialist Revolution the development of analytical chemistry in the USSR has been determined by two factors: by the peaceful development of analytical chemistry as a science, and by those problems placed before analytical chemistry by the demands of socialist construction in the Soviet Union. These conditions follow upon the position and organization of science in the USSR, and from the practical requirements of the social economy, in particular, by the metallurgical industry with special reference to ferrous and non-ferrous metallurgy. During these years analytical chemistry has developed to an extent unprecedented before. It is natural that its development has been closely related to the progress of industry as a whole.

The industry of our country was subjected to a particularly severe test during the second world war. Analytical chemists had to be accommodated in new places where they could not always get what was necessary. But, after the war, demands for quality control of production expanded at a rapid tempo. The earliest systematic research into analytical chemistry related to the control of production of platinum, iridium, rhodium, and other metals of the platinum group.

When industry started to adopt the high-melting metals beryllium, niobium, tantalum, titanium, tungsten, rhenium, zirconium, hafnium, the rare-earths, thorium, and uranium, new technological processes were necessary for separating and handling them; such methods were developed on the bases of the best analytical chemical schemes, also developed as a rule by analytical chemists.

The significant increase in work on analytical chemistry is closely related to the discovery and use of atomic energy. The search for the raw material – uranium – its analysis for impurities, the control of processes for isolating irradiated materials have necessitated completely new techniques. Not only have methods been developed for searching for uranium (and thorium) which were based on their radioactive properties, and on the capacity of the uranyl ion to luminesce in ultraviolet light, etc., but methods have also been developed for the analysis of pure uranium, as well as for separating and isolating plutonium and other transuranium elements, and radioactive fission products. The experience gained in the study of fission products, in its turn, has made it possible to make wide use of these radioactive products as labeled atoms.

Atomic industry demanded pure and ultrapure materials free from neutron-active materials. As a consequence of this it was found that, in general, ultrapure materials – in particular certain metals – acquire special properties e.g., semiconductor properties. Antibiotics and other materials which are very important physiologically, also demanded a high degree of freedom from impurity.

All this placed before analytical chemistry a completely new problem – the development of methods of control over impurities in the most diverse materials, at contents of these impurities of $10^{-7}-10^{-9}\%$. It must also be pointed out that this, in turn, led to new, powerful, analytical methods never known before, e.g., activation analysis, irradiation in powerful accelerators by various elementary particles, irradiation in a reactor, and many other radiochemical methods of determining impurities.

It is possible to carry on further with enumerating many other similar problems in the field of analytical chemistry which have arisen particularly during the recent years. The appearance of problems which are characteristic of our time has compelled analytical chemists on the one hand, to intensify main research on the study of systems of exceptional interest for analytical chemistry, compounds of the rare elements, fluorides, organic complexes, etc., and, on the other, where this was clearly desirable, to depart gradually from the classical methods of analysis. So-called instrumental methods of analysis have already found application in analytical chemistry; these include spectroscopy, x-ray spectroscopy, mass-spectrometry, oscillographic polarography, and many others. The requirements of science and industry have directed work to a considerable extent onto more automation of chemical control, the latter being realized with the aid of physical and physicochemical methods, e.g., absorption spectra of solutions, electrical conductivity, automatic gas analysis, etc. The greatest improvements have been achieved in the control apparatus used for gas analysis and pH-meters.

In this rather brief review of some of the most important scientific problems of analytical chemistry, one cannot omit reference to yet another series of methods which have been widely used in our time. We have in mind of course chromatographic analysis in all its aspects. An ion-exchange resin industry has been created, which is of great importance not only for analytical chemistry. The study of extraction processes in analytical chemistry has prepared the way for their use in industry.

Many highly sensitive organic reagents have been discovered which can be used for inorganic analysis; luminescence analysis has been widely used.

Microchemical techniques have unexpectedly acquired practical importance for scientific research purposes; instrumental methods have assumed immense importance in analytical chemistry. All forms of spectral analysis, both emission as well as absorption, have penetrated widely into factory practice and have frequently lightened the arduous work of the analytical chemist. Significant progress has been made in the field of x-ray spectroscopy. The development of original apparatus with curved crystals possessing high-focusing powers has enabled us to solve problems in the analysis of pairs of elements of similar chemical properties (Nb/Ta, Zr/Hf, Tr, U/Th, Sr/Ca, and many others).

Thermography, oscillographic polarography in its variants, interferometry, mass-spectrometry of stable isotopes for the analysis of gas mixtures have been taken up in factory laboratory practice.

Microorganic elemental analysis of C, N, and S, halogens, etc., has replaced macroanalysis. The analysis of functional groups of organic compounds has become an indispensable method for the study and control of organic raw materials. There is no doubt that the mutual exchange of methods in the various fields, e.g., in biology and metallurgy, has had a significant effect on their improvement and development.

Numerous research centers have been set up within industry, as well as in thousands of factory laboratories; the Russian reagent industry has been organized together with the industry for manufacturing and supplying chemical apparatus; numerous standards have been developed with the aim of unifying factory analysis and GOST requirements.

All this would have been impossible without the participation of a huge army of analytical chemists. Departments of analytical chemistry and higher schools have ensured the supply of thousands of such specialists.

The journals "Analytical Chemistry," "Factory Laboratory," and the abstract journal of the USSR Academy of Sciences "Chemistry" are published in the Soviet Union; the latter contains abstract of Russian and foreign literature on all questions relating to the theory and practice of analytical chemistry. During the period 1941-1952 alone about 8500 papers were published in Russian on analytical chemistry. The Institute of Analytical Chemistry was created within the framework of the USSR Academy of Sciences. The numerous annual conferences on individual problems in analytical chemistry have enabled analytical chemists to exchange scientific experience.

From the specialist reviews given below of some of the branches of analytical chemistry, it is clear not only how much has been done, but how many talented scientists – analytical chemists – there are.

PHYSICOCHEMICAL ANALYSIS OF ANALYTICAL SYSTEMS

I. V. Tananaev

During the last 20-30 years wide use has been made of physicochemical analysis, a discipline created by N. S. Kurnakov and his school. Physicochemical analysis which was developed for application the study of numerous metallic, salt, organic, and other equilibrium systems, did not originally attract the serious attention of analysts; the individual, sporadic investigations made along these lines were not interconnected. Nevertheless, dating from the conference on analytical chemistry in 1939, when the basic problems connected with use of physicochemical analysis in analytical chemistry were first formulated, the appropriate studies assumed a systematic nature. At present a vast amount of material has been accumulated in this field, by means of which, it has been possible to make some generalizations, and to formulate future developments in this, without doubt, very promising field.

In general, physicochemical analysis can be regarded as a branch of general chemistry in which a study is made of the properties of equilibrium systems in relation to their composition.

The basic requirement of physicochemical analysis is the parallel study of each given system by as many different methods as possible, with the aim of comparing a number of physical properties of the system in relation to its composition. In consequence, it has been found that not every method is capable of sensitively reflecting in due measure the chemistry of a system, while some individual methods do not explain it at all. When applied to the problems of analytical chemistry it especially should be emphasized that it is necessary to choose properties which react most sensitively on the chemistry during changes in the composition of the system. It is precisely for this reason that during the study of analytical systems on the basis of the techniques of physicochemical analysis, such methods as spectrophotometric, potentiometric, polarographic, chromatographic, and conductometric methods are often used. Such methods as determination of specific gravity, refractive index, viscosity, etc., are naturally of no interest for the study of the chemistry of analytical systems (particularly in dilute solutions).

The graphical method of treating experimental results has acquired great significance in physicochemical analysis; thanks to this method, during determination of the composition of reaction products, it is possible to present the results with the greatest simplicity and clarity. All the same, the graphical method has still not achieved that degree of development which would give, in all cases, not only a qualitative, but also a quantitative picture of interaction within a system. At present the graphical method is being used more frequently in conjunction with further mathematical treatment of experimental data, with the aim of searching for rational methods of calculating the appropriate constants which characterize the interaction.

During study by physicochemical analysis of systems of an analytical nature, two fundamental techniques have been predominantly developed: the study of isomolar mixtures, and the study of mixtures when the concentration of one of the components is a constant. The results in both cases can be regarded to a certain extent as the results of corresponding cross sections of the complete diagram of composition against property; nevertheless, as a consequence of the fact that in systems of analytical importance, chemical interaction is characterized by a relatively sharp displacement to one side, and much time is required to get the complete diagrams, the two techniques indicated have acquired independent significance. It is pertinent to note here that the method of isomolar mixtures which is widely used abroad, and has been called the Ostromyslensky-Zhob method in the Soviet Union (the method of continuous change), is a special case of physicochemical analysis, where isomolar series are used only as one of the methodological means of constructing a complete diagram of state for a system. At the same time it must be emphasized what an important part the Ostromyslensky-Zhob method has played in developing research related to the quantitative side of the evaluation of interactions in solutions (by calculating the instability constants of the reaction products of complex formation). The classical school of N. S. Kurnakov on physicochemical analysis has devoted relatively little attention to this question.

Despite the comparatively short period of development of research on the physicochemical analysis of systems of importance in analytical chemistry, a considerable amount of work has been carried out in Russian scientific institutions. The present review only covers the most important of the work carried out in order to indicate the main aspects of the question.

For the sake of convenience, homogeneous and heterogeneous systems will be considered separately below.

Homogeneous Systems

A study of the relation between composition and physical properties of systems is almost the only reliable method of studying interactions in solution. During a study of solutions by means of the techniques of physicochemical analysis, all stages of the reaction are reflected in the results of the study, irrespective of the composition and nature of the reaction products formed. In this connection, therefore, there is no sense in considering for example, simple and complex compounds formed in this or that system, as a generalized category of materials; under the experimental conditions used there is established between them a definite equilibrium (sometimes via compounds of intermediate composition), which can be shifted to one side or the other, in accordance with the ratio of reactants, their concentration, the temperature, and other variable conditions. The various reaction products acquire predominating importance according to what part of the diagram is being considered.

As a rule, diagrams of composition–state for solutions, do not give an exhaustive picture of the concentrations in a system made up of various reaction products, particularly during a significant shift of the reaction toward one side. In such a case, when the diagram of state –composition is constructed with the normal accuracy (e.g., 0.1% of the original concentrations of the components), it is not possible to represent on the diagram very small concentrations of components or reaction products (which are a few orders lower than the indicated limit), without resorting to logarithmic scales. The first published space diagrams – models – representing the process of formation in solution of silicomolybdic acid and platinum iodide (in the form of a sol) with subsequent transformation to the ion $[PtI_6]^{2-}$ can, presumably, serve as examples of real diagrams constructed by means of classical techniques. Unfortunately, little attention has been given to improving graphical methods of representing analytical systems.

A. K. Babko (1947) suggested a new method of constructing triangular diagrams for systems of the general type M-A-S (a central ion coordinated ion-solvent) with complex formation considered as a complex case of interaction, when several products (complexes) are formed in succession in the system. On this model it is possible alongside stoichiometric relations between components, to represent a field of "dominant" groups, the boundaries between which are determined by the relations: $[MA] > [M]$, where $A > K$ (the dissociation constant of the first complex). Thus the state of the system (from the point of view of the accurate values of the concentrations of all the constituents) is related to the values of the dissociation constants of the chemical reaction products formed in succession. The value of the property is plotted perpendicularly to the surface of the drawing, which makes it possible to construct space diagrams.

A. K. Babko has also suggested a method for constructing so-called equilibrium diagrams for systems of the type considered, which give a relation between reaction conditions and the equilibrium state of the system. For compiling such a diagram (the principles for constructing which has been given by Bjerum for multibasic acids), the primary results of the composition – property diagram, should be subjected to an appropriate mathematical treatment, on the basis of results on chemical stability (instability constants) of each of the interaction products. The equilibrium diagram shows the relation between the amount (in %) of the separate forms of the complexes (or the logarithm of the concentration of the central atom) and the logarithm of the concentration of the uncombined addendum. Examples of such diagrams have been given in the numerous papers of A. K. Babko (1945), devoted to the study of thiocyanate, salicylate, and pyrocatechol complexes of trivalent iron, and in the work of A. K. Babko and L. I. Dubovenko (1956) on the oxalate complexes of trivalent iron, aluminum, etc.

Despite the somewhat arbitrary nature of the individual ideas (expressing composition in the ionic forms of the components, the concentrations of which in the original solutions are not always accurately known; the absence of any indications of the limits of applicability of the methods of calculation based on the law of mass action, without resource to the values of the activities of the ions) proposed by A. K Babko, taken as a whole, the system of treating the experimental results obtained on the basis of physicochemical analysis of systems of an analytical character, and the way they are represented, mark an important step forward. This is particularly graphically illustrated in the case of the ionic system: $Fe^{3+}-SCN^{-}-H_2O$, for which a complete equilibrium diagram is given which represents the concentration ratios of the ions: Fe^{3+}, $Fe(SCN)^{+}{}_{2}$,* $Fe(SCN)_2^{+}$, $Fe(SCN)_3$, $[Fe(SCN)_4]^{-}$, $[Fe(SCN)_5]^{2-}$ and $[Fe(SCN)_6]^{3-}$. This study on the iron thiocyanates is one of the most comprehensive in the literature In the cited work of A. K. Babko and in other articles by him, one of the most important features is that the individual steps in complex formation in various systems are brought out, while the dissociation constants of the corresponding reaction products are calculated It should be added that A. K. Babko discovered a case of formation of a ternary compound in solution and worked out appropriate graphical methods of representation.

Using the optical method, and on the basis of physicochemical analysis, A. K. Babko and K. E. Kleiner were able, proceeding from the effect of fluoride ions on the color of the thiocyanate complex of iron ($Fe(SCN)^{2+}$), and of the capacity of Be^{2+}, Al^{3+}, Fe^{3+}, etc , to combat this influence on introducing them into the system, to postulate the formation of, determine the composition, and calculate the instability constants of fluoroberyllates from BeF^{+} to $[BeF_4]^{2-}$; fluoroaluminates from AlF^{2+} to $[AlF_6]^{3-}$; fluoroferriates, from FeF^{2+} to $[FeF_5]^{2-}$; and compounds of titanium and zirconium with fluorine. The principle of this variant of the optical method of determining instability constants of complex ions can be widely extended to other systems, e.g., instead of iron thiocyanate one can take iron salicylate; while instead of the fluoride ion, oxalate, phosphate, citrate and other ions can be taken.

To this work (the work of the Kiev school) can be related the systematic studies carried out by A. T. Pilipenko (1950); the latter, in particular, determined by means of physicochemical analysis the composition of the dithizonates of a number of metals (Tl, In, Ga, Ni, Co, Sn^{2+}, Bi, Cu^{2+}, Ag, Hg^{2+}, Mn and Fe^{3+}), and calculated their instability constants, and also established the composition of the phosphate complex of trivalent iron in solution.

Mention should be made of the monograph by A. K. Babko which was published recently (1955); this is a thorough and original work devoted to a study of complex formation on the basis of physicochemical analysis. This book summarizes the work carried out by A. K. Babko and numerous co-workers over a period of years on a study of interactions in solution based on the results of spectrophotometric methods.

Theoretical questions related to the application of physicochemical analysis to the study of interactions in solution, on the basis of the spectrophotometric method, have been developed by N. P Komar and co-workers Noteworthy are the methods they have developed for calculating the conditions under which the Ostomyslensky-Zhob method is applicable. The investigations carried out by V. P. Tolmachev and L. N. Adamovich are closely related to those of N. P. Komar. Physicochemical analysis of systems with colored compounds of divalent cobalt; of systems of nickel ions and 2-nitrose-1-naphthol in relation to pH; of the quinalizarinberyllium complex; of zinc with methyl violet and thiocynate, etc., belong to this category

This group of research workers (the Kharkov group) have concentrated on graphical interpretation of the results of physicochemical analysis of systems, on their mathematical treatment, and on the calculation of the instability constants of the reaction products, with special reference to calculation of such factors (usually not taken into account) as the hydrolysis of the central atom of the complex compound, the pH of the solution polymerization of ions and, in general, every side reaction. The corresponding conclusions are liberally accompanied by mathematical calculations and a complex system of designations, the interpretation of which requires special training, particularly in those very frequent cases where conclusions are given in a general form and are not connected with experiment.

The numerous and interesting researches carried out by K. B. Yatsimirsky and co-workers belong to this category of general and theoretical questions bearing upon the use of physicochemical analysis during studies of interactions in solution. Most of these papers, in addition to methodological questions, also contain theoretical interpretations, touching mainly upon the method of dealing with the experimental results obtained during determination of some property or other connected with complex formation, including stepwise complex formation.

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*As in original — Publisher's note.

The study of the process of formation of the amine complexes of copper and nickel by means of the optical density method belongs to this category. The important question of the displacement of the maximum (irrational maxima) on the property curves in isomolar series during the formation of certain complexes, is considered in this work. The use of the thermal effect of a reaction as a property, when stepwise complex formation occurs in a system, is a special feature of K. B. Yatsimirsky's work. In this connection mention must be made of the study of complex formation in the systems $NiCl_2-NH_3-H_2O$ and $CuSO_4-NH_3-H_2O$, and the determination of the heat of mixing and entropy, during formation of the oxalate complexes of a number of divalent metals.

The work of this last school (the Ivanov school) is characterized by its wide thermodynamic basis during treatment of results.

The work cited above relates predominantly to studies of optical density as a property of the system being studied. In some studies, carried out mainly in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, in the Institute of General and Inorganic Chemistry of the Ukrainian SSR Academy of Sciences, main emphasis has been placed on a more detailed study of systems with the aim of comparing results obtained by a number of methods carried out in parallel, usually spectrophotometric, electroconductivity, and e.m.f. methods. In these studies chief attention was given to developing methods of proving the actual formation of this or that compound in solution in complex systems, particularly when stepwise interaction occurs. Hitherto it has not been demonstrated that it is possible to explain all the stages of interaction in similar systems by direct study of composition– property diagrams. Bringing all these questions together is the object of physicochemical analysis. I. V. Tananaev and his co-workers (since 1945) have devoted their studies along these lines; they use the method of determining the concentration of the hydrogen ions liberated during interaction of various cations with weak acid, in order to establish the "natural" chemistry in the systems. Thus in corresponding systems containing HF, they were able to state that the ions BeF^+, AlF_2^+, InF^{2+} and InF_2^+, GaF_2^+ $ZrOF^+$, $[ZrF_6]^{2-}$ and other fluormetallates were formed in solution. Similar studies of interactions in systems containing beryllium ions and organic acids of various types enabled them to explain the rules of formation of the corresponding compounds of beryllium, and to determine the place of this metal in a number of other metal-complex forming agents.

Mention should be made of the thorough studies devoted to the reactions of formation of oxalates, tartrates, and nitrates of aluminum, molybdenum, and tungsten at various stages in the neutralization of the original oxalic and tartaric acids, and similar studies on gallium oxalates. An essential factor in these studies is the possibility of comparing the results obtained by the optical method (in the ultraviolet) with results obtained by electrical conductivity, e.m.f., and heats of reaction. When this is done, it has been shown very convincingly in some cases, that there is no possibility of establishing the chemistry of the system without taking into account the additive properties of the components of the system.

The interesting research work of Ya. A. Fialkov and co-workers (1956) has been devoted to a study of the mechanism of the interaction of certain metals with trihydroxyglutaric acid. From a methodological point of view this work is noteworthy because of the use made of the electrical conductivity method for studying solutions. The principles of this side of the question has been particularly emphasized in the article of I. A. Shek and Goldinov (1950), and later in those of Ya. A. Fialkov and Z. A. Shek (1956) and Muzyk (1956). All these studies, together with those cited above, testify to the fact that the electrical conductivity method, when used for physicochemical analysis of systems of an analytical type, may occupy an important place alongside other methods. While not being specific, and in some cases not sufficiently sensitive and accurate, the electrical conductivity method is nevertheless applicable in principle to all systems, and when reliably used (in the sense of a correct approach to taking into account the additive properties of the components of the system) and in the absence of a significant "background," which is determined by the presence of foreign materials in solution, may be of great service.

Investigations in which use is made of the polarographic method together with determination of composition, and calculation of instability constants of the reaction products in solution, occupy a separate place. To this category belongs the work of V. F. Toropova and F. M. Batyrshina (1949), who established the existence in solution of the ions $Pb(CH_3CO_2)^+$, $[Pb(CH_3CO_2)_3]^-$ and $[Pb(CH_3CO_2)_4]^{2-}$, the work of A. M. Vasilyev and V. I. Proukhina (1951), who made a study of systems consisting of Zn^{2+} and Cd^{2+} on the one hand, and Cl^- and Br^- on the other, and who calculated the instability constants for MeX^+, MeX_2, and $[MeX_4]^{2-}$, and some other researches.

Research work on the application of the polarographic method carried out with the same aim in view, but in which physicochemical analysis was not the basic means of solving the problem, are very numerous and cannot be considered here. The same is true of the chromatographic method, with respect to which investigations involving the use of the physicochemical method of analysis have not received the development which they deserve.

It is rather strange that physicochemical analysis has not yet found the application it should for studying extraction processes. Of studies belonging to this category mention should be made of the work by A. K. Babko and A. T. Pilipenko (1946), and that of I. M. Korenman and F. R. Sheyanova (1947), in which the methodological side of the question has been considered in detail. When combined with the use of labeled atoms these studies will, probably, receive considerable development in the nearest future.

Heterogeneous Systems

The importance of heterogeneous systems, or, in other words, systems containing precipitates, is very great in analytical chemistry; all the same, the appropriate reactions have been studied to a far lesser extent than have homogeneous systems by the physicochemical method. This can presumably be explained by the fact that the presence of a solid phase in heterogeneous systems assumes a preparative method of investigating the composition of the latter, as a result of which, studies of the chemistry of the system in this case have often been confined to determination of the composition of the solid phase by analytical methods. When this is done it is usually assumed that the chemistry of reactions in solution can be characterized by the help of stoichiometric coefficients established for the composition of the solid phase. The incorrectness of this approach, obvious long ago, is particularly emphasized in modern physicochemical studies, and in particular in studies on physicochemical analysis of heterogeneous systems, for which not only the solubility method has been used (this time, so to say, in dynamic conditions, when one remembers that the preparative method can be related to the category of static methods), but also methods of determining e.m.f., specific electrical conductivity, optical density, the volume of precipitates, etc.

Most interesting from the point of view of using physicochemical analysis for the study of heterogeneous systems of importance in analytical chemistry, are those studies in which the various properties of systems have been compared. Thus it is possible to call systematic, studies of systems of the type $\Theta^{n+} - Me_4[Fe(CN)_6] - H_2O$, in which there is observed a large variety in the composition of the so-called mixed ferrocyanides in relation to the nature and valence of the test metal ion (Θ^{n+}) and of the alkali metal in the original ferrocyanide $-Me_4[Fe(CN)_6]$. Mixed ferrocyanides, are, as a rule, sparingly soluble and determination of their composition by a comparative method would appear to be fully justified. Nevertheless, as experiment has shown, the composition of these compounds is sensitive to external factors and changes within wide limits. Consequently, physicochemical analysis would appear to be particularly effective for the study of the composition and properties of this class of compounds. It has been established that the following compounds can be formed: $K_4Ni_4[Fe(CN)_6]_3$, $K_4Co_{10}[Fe(CN)_6]_6$, $K_{12}Co_8[Fe(CN)_6]_7$ and $Cs_2Co[Fe(CN)_6]$, $K_2Mn[Fe(CN)_6]$, $MeLa[Fe(CN)_6]$, where Me-Li, Na, K, Rb, Cs, H and $\frac{1}{2}$ Ca, $\Theta_4[Fe(CN)_6]_3$ $Me\Theta[Fe(CN)_6]$ and $Me_4\Theta_8[Fe(CN)_6]_7$, where Θ = Ce, Nd, Y, Ga, In, Fe; $K_{16}Cd_{10}[Fe(CN)_6]_9$, $Tl_2\Theta_3[Fe(CN)_6]_2$, $Tl_4\Theta_4[Fe(CN)_6]_3$, $Tl\Theta[Fe(CN)_6]$ and a number of others. The properties of all these compounds are suitable for developing new analytical methods of determining the corresponding metals.

Investigations in the field of metal ferrocyanides have most convincingly demonstrated the expediency of using physicochemical methods of analysis during studies of complex reactions which occur with formation of several compounds within one system. In particular, it has been shown that all the variety of processes of formation of sparingly soluble mixed ferrocyanides can be depicted by means of four types of solubility diagrams, by means of which it is possible, to a significant extent, to forecast the path of the reaction in systems containing the given components. Studies have been made on the application of physicochemical analysis for investigating questions relating to the structure of "the outer sphere" of mixed ferrocyanides, using labeled atoms.

Similar studies of reactions which occur with formation of the hydroxides of various metals, have shown that in corresponding systems of the general type: metal salt – alkali – water, when there is a deficit of alkali, as a rule, formation of one or more basic salts occurs, the latter being converted into the normal hydroxides on addition of more alkali. Analysis of the diagrams obtained has made it possible to classify the processes of processes of formation of the hydroxides into three groups.

1) Only the normal hydroxide is formed in the system; basic salts are not formed. This type of diagram is observed in the system $AgNO_3-NaOH-H_2O$.

2) An insoluble basic salt is formed in the system, this basic salt is then converted into the normal hydroxide; this type is observed in such systems as $MeSO_4-NaOH-H_2O$, where Me = Zn and Cd.

3) First soluble and then insoluble salts are formed, which are further converted into the normal hydroxide; such a type is observed in systems containing gallium and thorium.

Although, to a certain extent, the indicated change in the form of hydroxide depends on the valence of the precipitated cation, nevertheless, individual gradations (according to the degree of basicity of the salt, or the difficulty with which it is converted into the normal hydroxide) are observed even within the limits of the group of cations with only one valence. These gradations, in a somewhat clearer form, can only be observed from the corresponding diagrams of the physicochemical analysis of the systems; preparative methods are only of limited significance in such cases (as in the case of ferrocyanides).

The general regularities in changes of composition of precipitates studied, taking metal ferrocyanides and hydroxides as examples, and also observed in other cases, e.g., in the system $AlF_3-NaF-H_2O$, where there is formed two solid phases: $11NaF \cdot 4AlF_3$ and $3NaF \cdot AlF_3$; in the system AlF_3-KF-H_2O in which $AlF_3 \cdot 2KF \cdot H_2O$ and $AlF_3 \cdot 3KF$ exist; in the system $PbSO_4-K_2SO_4-H_2O$, in which, in addition to $PbSO_4$, there is formed the salt: $PbSO_4 \cdot K_2 SO_4$, etc., Thus, changes in the composition of solid phases, as a consequence of changes in the concentration and ratios between the reactants, are more often the rule than the exception.

Changes in the composition of the solid phase can result not only from chemical transformations, but also in connection with other phenomena, for example adsorption and formation of solid solutions, which can be regarded as belonging to the category of coprecipitation processes. An attempt at investigating the phenomenon of coprecipitation by means of physicochemical analysis was made on systems including $BaSO_4$ as the solid phase. As a result of this it was shown that soluble sulfates can form solid solutions with $BaSO_4$; this capacity increasing from lithium to potassium and decreasing from potassium to cesium. Coprecipitation of cations with other valencies ranging from two to four, with $BaSO_4$ has also been studied.

Investigations of heterogeneous systems in which use has been made of physicochemical analysis have demonstrated the very complex character of solid phases, the characteristics of which, on the basis of accepted (but, in actual fact, far from being always justified) criteria like solubility product of precipitates can only be regarded as a crude approximation. The multitude of similar phenomena, sometimes, not chemical in nature, which nevertheless are reflected in the composition and properties of the solid phase, the frequent absence of "stoichiometric proportions" during the solution process (the nonequivalence of suggested ionic forms in a saturated solution) only allow one to regard similar criteria as very arbitrary. On the other hand, as a result of the fact that the method of physicochemical analysis is not yet used widely enough for studying heterogeneous analytical systems, no factual results are available on the basis of which existing theories could be corrected. All the same, an attempt at giving a rational classification of precipitation reactions based on ideas arising from experimental results obtained by means of physicochemical analysis of corresponding systems, has been made independently by I. V. Tananaev (1950) and A. K. Babko (1952).

Systems in which, in one medium or other, studies are made of the solubility of a solid phase whose composition is accurately known, also belong to the group of heterogeneous systems. Usually, in such systems, it is the practice to calculate the instability constants of compounds formed in solution on the basis of the solubility product of the solid phase, or by making the assumption that this regularity in its classical form obeys the law of mass action. To this category belongs work on the determination of $K_{AlF_2^+}$ on the basis of the solubility of CaF_2 in solutions of ammonium salts; calculation of the composition of cerium oxalate on the basis of the solubility of $Ce_2(C_2O_4)_3$ in HNO_3 and H_2SO_4 solutions, and of $Ce_2(C_2O_4)_3$ in $H_2C_2O_4$ solutions, and a number of other similar results. The use of labeled atoms in such investigations should be of essential importance; hitherto, however no data has been accumulated along these lines which are deserving of note. No doubt development in this field will be intensive.

Separate mention must be made of the method of measuring the apparent volume of precipitates, by means of which it has been proven possible to characterize the chemistry of heterogeneous systems. This method, suggested by I. V. Tananaev (1950) has been used for studying a number of precipitation reactions, in particular formation of basic salts and hydroxides of: beryllium, aluminum, silver, zinc, and cadmium, gallium, thorium, indium, silver phosphate, the mixed ferrocyanide of lanthanum and potassium, lead iodide, and others. The method, being very simple to carry out, makes it possible to establish the composition of a precipitate and also to observe such phenomena as complex formation (formation of double salts), formation of solid solutions, polymorphic transformations, etc, during precipitation.

The use of the light absorption method as applied to the study of heterogeneous systems is worthy of attention. The possibilities of this method are much wider than the aggregate effect which has already found application in the form of so-called turbidimetric or heterometric titration. Studies of precipitation reactions by the light extinction method * on the basis of physicochemical analysis have shown that determination of the composition of the precipitate formed in a system (e. g., in isomolar series) can usually be carried out despite the polydispersivity of the latter. More detailed study of light extenction in heterogeneous systems during changes in their composition has made it possible to establish a presumably general for all precipitates, relation between the percentage dispersivity and the solubility of presumably all precipitates; this relation is expressed by a curve with a maximum, determined by the fact that for two extreme values of the degree of dispersivity (agreggation) of the precipitate material (a molecular solution and monocrystals) the light extinction is a minimum and (for colorless precipitates) is practically equal to zero. Just as the solubility of a precipitate in the test system changes within wide limits (in particular, for a constant content of the component which is precipitated in the original mixture), so may the light extinction of the system (for one and the same weight of precipitate) assume values within the same and even wider limits. On the basis of work carried out along these lines, it follows that the widely held opinion that the sensitivity of a precipitation reaction, [according to the results of visual observation (the turbidity of a solution)] is greater, the lower the solubility of a precipitate, is only partly true. The light extinction of a given precipitate increases during a decrease in its solubility only to a certain limit, after which it again decreases and the reaction becomes "insensitive." In such cases, in order to increase the sensitivity of the reaction, it is necessary to increase the solubility of the precipitate artificially (e.g., the solubility of AgI by means of NH_3 or KI). Having determined, the conditions for maximum light extenction for a given mass of precipitate, (by means of physicochemical analysis), it is possible to speak of the coefficient of molar extinction with respect to suspensions. In the opinion of the author of the present article, at the present level of turbidimetric analysis, the results obtained by means of physicochemical analysis of heterogeneous systems, in which use is made of the light extinction method, may ensure an essential development of this very important field.

Amperometric titration when applied to a study of analytical systems may play an important part in understanding precipitation processes. Despite the very large amount of work carried out along these lines, the physicochemical method of analysis has only started to find application. Thus, systems of copper or uranyl ions have been studied on the one hand, and the ferrocyanides of various alkali metals on the other.

Finally, at the end of this brief report, we may conclude that studies in the field of physicochemical analysis of systems which are, or could be, of importance in analytical chemistry, are being developed intensively at present both in the Soviet Union and abroad. Much of the work which has been carried out along these lines has proved useful not only in providing a deeper understanding of the nature of the corresponding processes, but also in practice. Nevertheless, it is essential that in the immediate future even more questions of a theoretical and methodological nature must be cleared up, and that the number of individual methods used for research must be increased.

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* We have in mind studies in transmitted light on the principle of normal spectrophotometry. The aggregate effect determined by absorption and scattering of light is here called light extinction (in contrast to homogeneous systems). Studies of systems based on light scattering (the nephelometric method) are not considered.

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THE APPLICATION OF RADIOACTIVE ISOTOPES IN ANALYTICAL CHEMISTRY

I. P. Alimarin and N. A. Rudnev

The development of studies on radioactivity in the Soviet Union is closely connected with the names of the famous Russian scientists V. I. Vernadsky and V. G. Khlopin. Academician V. I. Vernadsky who saw the exceptional importance of radioactivity for the development of physics, chemistry, geology, and the other sciences, as long ago as 1909, guided work on the study of certain minerals with the aim of getting radium from them. In 1922, after organizing the State Radium Institute, a vast amount of work was carried out on radioactivity. In this way the Soviet school of radiochemists arose; this showed a huge effect on the development of problems in nuclear chemistry in the Soviet Union.

The intensive studies of our scientists in the field of nuclear chemistry and the incidence of radioactive isotopes for almost all the elements in D. I. Mendeleev's periodic table have exerted a great influence on the solution of many important questions in analytical chemistry. At present, the method of radioactive indicators, which possesses exceptional sensitivity and simplicity, is one of the most promising methods in chemical research.

Initially, studies on the use of radioactive isotopes in chemical analysis received were first developed in the Institutes of the USSR Academy of Sciences, particularly in the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry under the direction of A. P. Vinogradov. Subsequently, the method of "labeled" atoms started to find wide application in many factory and scientific research laboratories.

In 1953, at the All Union Conference on the use of radioactive isotopes in analytical chemistry, results of studies were heard and discussed and the paths for future development laid down.

Soviet analytical chemists presented a number of reports on the use of radioactive isotopes in chemical analysis at the International Conference on the Peaceful Uses of Atomic Energy held in 1955 in Geneva.

Radioactive isotopes have acquired particular importance for solving a number of problems in chemical analysis in connection with the need for increasing the sensitivity and the rapidity with which analytical methods can be carried out. Radioactive isotopes have been used in analytical chemistry in solving theoretical questions, in developing methods of separating and detemining elements, and also in chemical technology.

Radioactive isotopes have been successfully used in studying the composition of materials at extremely low concentrations, in determining the solubility of precipitates, and in investigating the structure of complex compounds and their stability.

Radioactive isotopes have also been used in separating elements by precipitation, extraction, distillation, and in chromatographic analysis. The last of these methods has been particularly strongly developed, and its importance is increasing in connection with the possibility of separating elements with similar chemical properties.

The attention of research workers is being drawn at present to other special methods– methods of isotope dilution, radiometric titration, and the use of reagents containing labeled atoms, radioactivation analysis, quantitative analysis based on neutron absorption and intensity of reflected β-radiation.

Radioactive isotopes have made it possible to improve chemical analytical control in factory laboratories, and to develop new methods as well as improve existing methods for preparing specially pure reagents.

The main direction taken by research at the moment is connected with the problems of separating and determining extremely small amounts of elements, for example, during studies of nuclear fission products. A knowledge of the properties of materials at ultra-low concentrations helps in the successful completion of such work.

Systematic studies on the state of radioactive elements in dilute solution are being carried out in the V. G. Khlopin Radium Institute.

The work here is connected with solving the basic problem of whether it is possible to determine radioactive elements at very high dilutions in a colloidal state.

Considerable attention has been devoted to the study of radiocolloids both abroad (M. Curie, Hahn, Heysinsky) and in the Soviet Union.

The work of I. E. Starik and N. A. Alekseenko (1956), has shown that polonium at a pH of 7-10 gives colloidal solutions as a result of hydrolysis and the attainment of the solubility fraction of the products formed. Similar work has been carried out on the state of uranium in ocean water.

A. P. Ratner, N. G. Rozovskaya, and V. Gokhman (1957) have carried out some experiments from which we have gained a deeper understanding of the nature of radiocolloids. They have shown that in solutions of polonium and thorium isotopes (UX$_1$ and RdTh) there are two groups of particles with dimensions of the order of several dozen microns and around 1$\mu\mu$ respectively.

On the basis of these results the suggestion has been made that the coarsely dispersed particles are radioelements adsorbed on impurities, while the finely dispersed particles are formed by the radiocolloid itself. It is of interest to note that the fine particles do not pass through a dialyzator, while the radioelement found in the form of the coarsely dispersed particles does pass through a dialyzator, although only slowly.

The state of radioelements in solution has also been studied by the radiographic method (I. E. Starik and co-workers).

B. A. Nikitin and O. Ertsbakher (1932) have shown that formation of radiocolloids has an important effect on the value of the solubility of radium sulfate.

In an article published recently by I. E. Starik, A. P. Ratner and co-workers (1957), results were given of studies on the state of Zr, Tl^{I}, Tl^{III} in solution. It was found that in zirconium solutions of 10^{-11} mole/liter at a pH of 4.2, there is formed a negatively charged sol and the solubility product of $Zr(OH)_4$ is reached.

The authors established differences in the laws governing the adsorption of Tl^{I} and Tl^{III} on glass at various pH values. It was found that there is an interrelationship between the adsorption of Tl^{III} and its colloidal state. The approximate value of the solubility product of $Tl(OH)_3$ was calculated.

Valuable research has been carried out by A. K. Lavrukhina (1955-1957) in connection with the development of methods of separating radioactive isotopes obtained during bombardment of elements by various particles in accelerators. Studies have been made of the behavior of a large number of elements at very small concentrations during their separation by precipitation, extraction, electrolysis, and distillation.

The use of radioactive isotopes has opened up new possibilities for determining the solubility of analytical precipitates. The exceptional sensitivity and ease with which it can be carried out are the advanta of this method. Electrolytes which are in solution do not interfere with the determination.

As long ago as 1917 Vl. I. Spitsin determined the solubility of various thorium salts [$Th(C_2O_4)_2 \cdot 6H_2O$, $ThP_2O_6 \cdot 11H_2O$] and ThO_2 in acids, alkalis, salt solution, and also of $ThF_4 \cdot 4H_2O$ and $K_2ThF_6 \cdot 4H_2O$ in water. Subsequently this method was used by a number of research workers. I. Spitsin and co-workers determined the solubility of calcium molybdate using Mo^{99}.

V. V. Fomin, K. B. Zaborenko, and M. G. Kolesnikov (1952) determined the solubility of lead molybdate by means of Pb^{212}.

Radioactive isotopes have also found application in the study of the rate of isotopic exchange in a homogeneous medium between ions in solution and addenda of complex compounds, so that it is possible to judge their structure and stability.

Studies along these lines were started by A. A. Grinberg and co-workers as long ago as 1939, and have been systematically followed through up to the present.

A. A. Grinberg and F. M. Filinov (1939, 1941) studied the rate of isotopic exchange of complex bromides of divalent and quadrivalent platinum with bromine ions. This study showed the functional equivalence of bromine in the complex ions: $[PtBr_4]^{2-}$ and $[PtBr_6]^{2-}$, and also that exchange of bromine ions does occur in such a system. In the case of the central atoms of complex compounds it was demonstrated that there is almost complete absence of ion exchange, e.g., in the case of the system: $[Pt(NH_3)_2Cl_4] + K_2[Pt^*Cl_6]$.

In subsequent studies, A. A. Grinberg and his associates (1955) established a number of important ideas relating the rate of exchange of ions with the trans effect and the breakdown of complex anions.

In the work by A. E. Polesitsky (1939) the equivalence of the halogen bonds in the following compounds was demonstrated: K_2HgI_4, $AuBr_3$, $CuBr_2$, PBr_5.

I. V. Tananaev and M. I. Levina (1957) using the isotope Ag^{110} investigated the substitution reaction of the heavy and alkali metals in mixed ferrocyanides. In this way the relative stability of the bonds of the metals of the outer sphere of mixed ferrocyanides with ferrocyanide ions was established.

Separation of Elements

Radioactive isotopes have come to occupy a place of special importance in the study of the processes of formation of precipitates, and the phenomena which accompany the separation of a solid phase. Together with foreign research workers (Hahn et al.), Russian workers have contributed greatly to the study of such questions.

The classical work of Academician V. G. Khlopin and his co-workers (B. A. Nikitin, A. E. Polesitsky, A. P. Ratner, and P. I. Tolmachev) as long ago as 1922 established the basic rules in the phenomena of coprecipitation by means of labeled atoms. This field is at present being successfully developed by V. G. Khlopin's co-workers, M.S. Merkulova and V. I. Grebenshchikova.

G. N. Yakovlev and D. S. Gorbenko-Germanov (1955) have suggested a new method of isolating americium by coprecipitating it with potassium uranyltricarbonate and potassium plutonyltricarbonate.

G. I. Gorshtein and co-workers (1954) are studying the coprecipitation of cations with various precipitates, and use this process for purifying reagents.

V. P. Shvedov (1947, 1948) using the isotopes Ca^{49} and Na^{24} has studied the complete separation of calcium from magnesium and sodium as CaC_2O_4.

A research using physicochemical analysis has been carried out by I.V. Tananaev and A.I. Ulyanov (1950) for studying coprecipitation of the sulfates of the alkali metals Li, Na, K, Rb, Cs, and NH_4 with $BaSO_4$.

V. B. Miller, M. B. Neiman, and L. A. Sazonov (1952) have also used the method of physicochemical analysis involving the use of radioisotopes for studying coprecipitation.

The study of coprecipitation by physicochemical analysis (the method of isomolar mixtures) in conjunction with radioisotopes has been suggested by A. K. Babko and M. I. Shtokalo (1955) and has been used in the case of the coprecipitation of antimony with manganese dioxide.

Coprecipitation of various cations with metal sulfides and methods of preventing such coprecipitation has been systematically studied in I. P. Alimarin's laboratory (N. A. Rudnev and A. A. Mazur) (1953-1957). New regularities have been established and the part played by crystallization and formation of chemical compounds has been demonstrated in these phenomena.

Recently, V. I. Kuznetsov (1954) suggested organic coprecipitants for concentrating traces of elements. The theory of the mode of action of this type of collector has been developed and coprecipitants have been suggested for a large number of metals.

Interesting studies on the use of complex organic compounds as collectors have been carried out by I. M. Korenman and co-workers (1955).

Investigations of a theoretical and applied nature in the field of extraction, involving the use of radioactive isotopes, are being carried out in various institutes and laboratories.

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* Analytical Chemistry, No. 5.

Some interesting work is being carried out by V. I. Kuznetsov and co-workers (1954); they have given a theoretical explanation of the extraction method and have developed a number of techniques for extracting various elements.

Extraction of inner complex compounds has been studied by I. M. Korenman and F. R. Sheyanova.

I. P. Alimarin and I. M. Gibalo (1957), using Nb^{95}, Ta^{182}, W^{185} have developed a method of separating niobium from tantalum and tungsten.

V. M. Vdovenko and co-workers have been studying the distribution of the nitrates of various metals between aqueous solution and organic solvents.

N. P. Rudenko (1948) has used extraction for preparing ThB, ThC, In^{115} in a radiochemically pure state without carriers.

A method of extractive separation of technetium from rhenium molybdenum, and ruthenium has been developed by Yu. B. Gerlit (1955).

K. V. Troitsky (1955) has studied extraction of the thiocyanate complex of tungsten, and of niobium cupferronate, using the isotopes W^{185} and Nb^{95}.

Ion exchange chromatography has been developed to a very large extent in recent years; this technique means that elements with similar chemical properties can be separated.

A large amount of work on the separation of nuclear transformation reactions as well as on the separation of a complex of elements, and the preparation of radiochemically pure materials has been carried out in research institutes and factory laboratories.

The successful accomplishment of such work is connected with the use of radioactive isotopes, by means of which it is possible to find the optimum conditions for separating elements.

Systematic research on the use of chromatographic analysis for analytical and preparative purposes has been carried out by D. I. Ryabchikov and M. M. Senyavin (1949-1957).

By using partition chromatography on paper in conjunction with the radioisotope Hf^{181}, N. S. Poluetkov (1955) separated zirconium from hafnium.

The state of radioelements in solution has been studied by means of ion-exchange resins, and the dissociation constants of complex compounds have been determined.

Separation of the radioactive isotopes of the rare earths by means of ion-exchange chromatography has been achieved by F. I. Pavlotska and A. K. Lavrukhina (1956). The method has been used for studying the isotopes of these elements formed as the result of the fission of uranium, thorium, and bismuth by high-energy protons.

N. P. Rudenko (1955) has successfully used chromatographic analysis for separating various radioactive isotopes.

Recently, A. K. Lavrukhina and F. I. Pavlotska (1957), using ion-exchange chromatography, separated promethium in quantitative amounts from uranium fission products.

Methods for the Quantitative Determination of Elements

Among new radiochemical methods, the attention of Soviet analytical chemists has been drawn to the isotopic dilution method of Hevesy and Khobbe.

The normal techniques for separating elements—precipitation, electrolysis, extraction, distillation lie at the basis of this method. The characteristic of this method is the absence of any necessity to separate the elements quantitatively. This makes it suitable for rapid separation and determination of elements— analogs.

I. E. Starik (1933) in this way determined $10^{-3}\%$ of lead in granites.

A detailed and systematic study of the isotopic dilution method has been carried out by I. P. Alimarin and G. N. Bilimovich (1955-1957).

The authors have developed a technique for determination of lead and bismuth when present together. These metals are precipitated as the benzenesulfonates and are subsequently extracted with isobutyric acid. Nb and Ta have also been separated from zirconium with subsequent determination of the first of these elements with benzeneselenious acid.

N. I. Polevaya and S. L. Mirkina (1955) have determined small amounts of rubidium in the presence of potassium by the isotopic dilution method.

In connection with the use of the radioactive isotopes of almost all the elements in the Periodic Table, the possibilities of using precipitation reactions in titrimetric determinations have been widely expanded; on this basis it has been possible to develop a new method — radiometric titration.

As a result of work by I. P. Alimarin, I. M. Gibalo, and I. A. Sirotina (1955-1957) a method has been developed for determination of beryllium and zirconium in the presence of aluminum and other elements by titration with phosphate. These authors have also determined thallium by means of Tl^{204}. Potassium iodate, phosphotungstic acid, and sodium tetraphenylboron have been used as the titrants.

I. M. Korenman and co-workers (1956) determined zinc and copper when present together by titration with potassium ferrocyanide using Zn^{65} and indicator. The method is also applicable for their determination in certain alloys.

Radioactive reagents are also being used at present in analytical chemistry. The method is based on precipitation of the test element with a suitable reagent containing a radioisotope. Measurements of the activity of the precipitate or solvent allows the content of the element to be determined.

The method of radioactive reagents means that it is possible to carry out determinations without having to weigh and to wash the precipitates free from impurities, or convert them into a quantitative form. Using this method it is possible to determine various organic materials, for example amino acids in their mixtures.

An interesting research has been carried out by I. V. Tananaev and A. M. Efremova (1955). They developed methods for quantitative determination of various elements (Al, Ga, In, Ce, Zr, Bi, Fe and U) by precipitation with Na_2HPO_4 containing labeled phosphorus. In this way it is possible to determine aluminum in magnesium alloys, and indium in concentrates. The method is highly sensitive and is rapidly carried out.

I. M. Korenman and co-workers (1955) have suggested a sensitive method for determination of potassium in refractory clay, feldspar, and other materials by precipitation in the form of nitrocobaltiates using Co^{60}.

Radioactivation methods enable about 10^{-11} g of an element to be determined. This method was suggested by Hevesy and Levy (1936-1938), by Seaborg and Livingwood (1938) and has been systematically developed by Boyd and Smailes. It was used for the first time in 1940 in the USSR by A. A. Grinberg for determination of iridum in platinum after bombardment with a neutron beam.

In recent years Soviet analytical chemists have been in a position to use nuclear reactors with intense beams of slow neutrons, so that it has become possible to develop new analytical methods.

I. P. Alimarin and Yu. V. Yakovlev (1953-1957) have, in the course of some years, carried out studies on radioactivation analysis. The objects of their studies were metallic germanium, bismuth, and graphite, in which they determined impurities in the form of other metals. P. D. Gorbachev using the radioactivation method, determined various impurities in beryllium, bismuth, and lead. A. I. Kulak has determined traces of various elements in Au, Ag, Ni, and Sb.

Two other methods must be mentioned which are distinguished by the speed with which they can be carried out, and by the possibility of carrying out an analysis without destroying the test sample. We refer of course to the method of analysis based on absorption of neutrons, and on the basis of the intensity of reflected β-radiation.

A. Ratner, G. Rik, and A. Shebashev (1955) have determined cadmium in alloys. V. I. Baranov (1957) and co-workers have developed a new and fairly accurate and rapid method for determining boron in samples of minerals; their method is based on neutron absorption by this element.

The analytical method based on intensity of reflected β-radiation was suggested by A. A. Zhukhovitsky (1951). It is based on differences in the capacity of the elements to reflect β-particles; the extent of the reflection depends on the atomic number of the element, and increases with increases in atomic number. N. A.

Bogdanov and V. F. Funke (1955) using this method have analyzed alloys of chromium with niobium, and of iron with tungsten.

The method deserves attention since it allows an analysis to be carried out rapidly.

V. B. Gaidadymov (1956) has developed a technique for determining lead in lead glass. Research has also been carried out on the application of the method to the analysis of binary mixtures (Nb– Ta; Mo– W).

Methods of analysis based on the use of radioactive isotopes and radioactive radiation, will, in the immediate future, be developed to an even greater extent for solving theoretical and practical problems in analytical chemistry.

EXTRACTION METHODS FOR SEPARATION OF ELEMENTS

V. M. Vdovenko

Extraction methods of separating elements based on the partition of materials between two practically immiscible liquids, combined with the techniques of coprecipitation, ion-exchange, electrochemical separation, and distillation, have found wide application in analytical chemistry. The advantages of extraction methods of separating elements are their high selectivity, the speed with which they can be carried out, the possibility of separating test materials from large amounts of other elements, and the simplicity of the apparatus.

As a result of the small area of the boundary separating the phases, and the absence of precipitates, it is possible, using extraction methods to isolate traces of elements, a separation which cannot be carried out by precipitation methods. Due to the high partition coefficient of the material to be extracted, it is often possible to concentrate the element to be extracted from dilute solutions.

Russian research workers have contributed a great deal to the development of the theory and practice of extraction separation of the elements. Together with foreign workers, Russian analysts have published review articles (A. K. Babko, 1950; V. I. Kuznetsov, 1954; A. V. Nikolaev, 1956). In these articles consideration is given to the chemical side of extraction processes and to the mathematical treatment of experimental results, whereby it is possible to determine the composition, and instability constants of compounds extracted in organic solvents, and to choose the optimum conditions for carrying out extraction separation.

In his review, V. I. Kuznetsov (1954) has given a most comprehensive bibliography which includes 460 references.

It should be noted that much of the work indicated subsequently which was carried out in scientific research institutes and factory laboratories, is not only of theoretical but also of practical importance for the social economy.

Theoretical Research Work

Important studies on the theory of extraction were carried out by A. A. Yakovkin as long ago as 1895.

While carrying out an experimental investigation on the distribution of iodine between water and carbon disulfide, A. A. Yakovin, despite the well-known results of Berthelot and Jungfleisch, which were put forward as experimental proof of the law of distribution of a compound between two immiscible solvents, was unable to confirm either the independence of the partition coefficient of iodine between water and carbon sulfide, and concentration, or the numerical results obtained by Berthelot and Jungfleisch.

This constancy of the partition coefficient was not found in other instances either, e.g., for the partition of iodine between water and bromoform.

Further theoretical and experimental study of the question showed that if the dissolved material is in an associated or dissociated state in one of the solvents, this complicating factor can be taken into account either by substituting concentrations by activities, or by introducing into the partition equation a coefficient determined graphically on the basis of experimental results. The equation then assumes the following form: $C_1^n/C_2 = \text{const}$.

Here C_1 and C_2 are the concentrations of the material distributed between the two phases. This equation is a quantitative expression of the partition law of Nernst-Shilov (M. Kh. Karapetyants, 1949).

N. A. Shilov and L. K. Lepin (1920) in their interesting studies on the distribution of a material between two solvents and the force field of a solution, also came to the conclusion that "the constant partition coefficient between two liquid phases, equal to the ratio of the individual solubilities, is a hypothesis which is neither a general law nor even an ideal limit, but only a very special case." According to their definition, "the partition coefficient in the general case, in the limit, is not equal to the ratio of the solubilities in two phases taken separately, but is equal to the ratio of the solubilities for equilibrium between all three phases (ternary point).

Thus Russian research workers already long ago have introduced essential corrections into the ideas according to which the partition coefficient of a material is equal to the ratio of the solubilities of the material in both liquid phases

Other important research has been carried out on extraction theory and solubility, which is related to it, by Russian workers.

V. K. Semenchenko and M. N. Shakhparonov (1948) tried to establish a connection between the dielectric constant of a solvent and its capacity to dissolve various materials.

Nevertheless, their theory is far from being experimentally verified in all cases. Thus, A. A. Grinberg and E. P. Zemlyakova (1948), showed that the complex $[Pt(NH_3)_4]\cdot[Pt(SCN)_4]$ shows the following characteristic behavior: it does not dissolve in water or acetone but dissolves in a mixture of the two. The authors explain this effect by the presence of an "affiliated solvation," when one part of the complex molecule is preferentially solvated by one of the solvents, while the other part of the molecule is solvated by the second solvent, and the sum of the partial energies of solvation of the individual components of a given compound is higher than the crystalline energy of the lattice, as a result of which the salt dissolves. It is suggested that the $[Pt(NH_3)_4]^{2+}$ ion is preferentially hydrated, while the SCN is solvated by acetone.

This research also shows that if the dielectric constant of a solvent were its basic characteristic, then the solubility in a mixture of water and acetone, which has a mean value for the dielectric constant, should not be greater than the solubility of the salt in each of the components of the mixture taken separately. The phenomenon of "affiliated solvation" undoubtedly does occur during extraction, particularly when mixed solvents are used.

S. V. Gorbachev and E. Ya. Mindovich (1953) studied the distribution of picric acid between water and nitrobenzene. The interesting feature of this work is the fact that nitrobenzene and water are characterized by high dielectric constants (the respective values for water and nitrobenzene are 79.45 and 34.89). At the same time the solubility of one liquid in the other is small. At 20°, the solubility of nitrobenzene in water is 0.19% wt., while that of water in nitrobenzene is 0.24 % wt. When one compares the dipole moments we get 1.84 Debye units for water and 3.95 Debye units for nitrobenzene. Dielectric constants and dipole moments characterize the value of the dielectric field of force within the dielectric. One might expect the partitioned material – in this case the strong electrolyte picric acid – to dissociate not only in water and aqueous media, but also in a nitrobenzene medium. Thus, the distribution in the test case will be of a very complex nature in view of the fact that not only neutral molecules of picric acid will be found in both phases, but individual ions as well. Treatment of the experimental data made it possible to establish the temperature and concentration relationships of the partition coefficient, and to find graphically the value of the change in potential energy during the transfer of one mole of picric acid from one phase into the other.

Interesting work in this field was carried out by B. V. Nekrasov and V. V. Ovsyankina (1941) during the study of the distribution of ferric chloride between water and ether. Analytical study of the ethereal layer during extraction of ferric chloride from aqueous solutions by ether showed that over a wide concentration range of ferric chloride and excess hydrochloric acid, the main component extracted appeared to be a complex acid $H[FeCl_4(OH_2)_2]$ which was fairly stable even in fairly concentrated aqueous solutions. In the absence of excess hydrochloric acid (or at relatively low concentrations of this acid) another complex acid $H[FeCl_3(OH)(OH_2)_2]$ was extracted in addition to the one already mentioned. On the other hand, when a considerable excess of hydrochloric acid was present in the original solution, the complex acids $H_2[FeCl_5OH_2]$ and $H_3[FeCl_6]$ started to be extracted.

V. I. Kuznetsov (1954) has developed the chemical theoretical basis of the extraction method of separating the elements. He distinguishes the following cases of extractive removal of the elements.

I. Extraction of the Elements in the Form of Oxonium or Amine Salts. According to this mechanism only those elements are extracted which, under the extraction conditions used, are present in the form of anions such as $FeCl_4^-$, or $SbCl_6^-$. The extracting solvent should, under the extraction conditions used, form oxonium cations in the case of oxygen containing solvents, or ammines when amines are used for extraction.

II. Extractions Based on Loss of Affinity for Water. According to this mechanism inner complex salts formed between the elements and organic reagents are extracted; such complex salts are the 8-hydroxyquinolates, dithizonates, cupferronates, dialkyldithiocarbamates; normal salts containing a large organic component part are also extracted, for example, salts of stearic acid, etc.

III. Extractions Based on "Physical Distribution." These occur in cases where the material to be extracted is soluble both in water and in the solvent which is immiscible in water, and forms nonsalt-like compounds with them. Such cases are relatively rare.

Extraction can be carried out successfully by using organic oxygen-containing compounds, having carbonyl oxygen (ketones, aldehydes, esters), since carbonyl oxygen is more inclined to form oxonium salts than ethereal oxygen. Since this process is related to the formation of oxonium salts, then only those elements which are capable of forming complex anions under the experimental conditions used, are extracted.

The positive influence of the presence of a carbonyl oxygen in the solvent molecule has been illustrated in the case of extraction from hydrochloric acid solutions of trivalent iron and quinquevalent vanadium (V. I. Kuznetsov, 1947, 1952).

V. I. Kuznetsov has carried out interesting researches into the theory of extraction.

V. I. Kuznetsov and E. V. Mitrofanova (1956) have shown, taking as examples the extraction of mercuric chloride by members of the homologous series of normal alcohols and methyl-n-alkylketones, and by mixtures of the lower members of the series and n-heptane made up to imitate the previous series, of pure individual solvents that the extracting effect of the mixtures of solvents is practically the same as the extracting effect of the individual solvents for an equal ratio of the amount of oxygen to carbon in each case.

Extraction Techniques in Analytical Chemistry

An original, improved, estraction technique has been suggested by V. I. Kuznetsov and I. V. Seryakova (1957). They used solid but low-melting mixtures of the usual solvents with paraffin and other materials, instead of the normal liquid extractants. Extraction was carried out in slightly warmed solutions when the mixtures used were liquid. The flask was then cooled, the melt allowed to solidify and stick to the walls of the flask so that is was possible to remove the aqueous phase simply by pouring it off. Extraction is carried out rapidly under such conditions in normal flasks and tubes.

Extraction methods in general cut down the time of analysis considerably. This is particularly evident from the work of Yu. A. Chernikhov, R. S. Tramm, and K. S. Pevzner (1956) on the separation of tantalum from titanium. The authors used fluoride compounds for extraction, the extractant being cyclohexane which removed tantalum fairly completely.

Instead of the 3-5 days which repeated precipitation with tannin takes, the time was cut down to a few hours by using the extraction variant.

Extraction of trivalent iron from hydrochloric acid solutions with diethyl ether, which has been used earlier, was improved by substituting the unsuitable diethyl ether by isoamylacetate (V. I. Kuznetsov, 1947), the latter being less hazardous from a fire point of view, and also extracts iron more completely. Extraction of iron with isoamyl acetate is now generally used both in Russian and abroad.

Extraction is widely used by Russian analysts during photometric determinations.

Iron thiocyanate complexes in alcoholic and acetone solutions have been studied in detail photometrically by A. K. Babko and V. S. Kodenskaya (1947); Subsequently, using physicochemical analysis, these authors established that of the various complexes formed in the aqueous phase, the complex which is most strongly extracted by ethyl acetate and other solvents is the complex containing the anion $Fe(SCN)_4^-$ (1951). The authors found that mixtures of alcohols and ethers dissolve a number of complexes found in the aqueous phase, and that mixed solvents are better extractants than each component taken separately.

The use of extraction for more complex thiocyanate complexes such as the ternary complex which contains copper, thiocyanate, and pyridine (Py) is also known. The complex $CuPy_2(SCN)_2$ is readily extracted by chloroform and is used for photometric determination of copper. Yu. Lure and L. B. Ginsberg (1939) have used this method for determining copper in flotation residues and in very poor ores.

R. I. Alekseev (1945) has used extraction of the molybdenum heteropolyacids of phosphorus, arsenic, and silicon, for separating these elements.

Yu. Yu. Lure and N. A. Filippova (1953), for the extraction-colorimetric determination of antimony, used extraction of the salts formed by the cation of methyl violet and the anion $SbCl_6^-$, while I. P. Alimarin and R. L. Podvalnaya (1946) used extraction of niobium in the form of the salt of the acid $H[NbO(SCN)_4]^-$ for the photometric determination of niobium.

N. K. Kuskova (1947) has developed a photometric method which enables from 0.005 to 0.15% of aluminum to be determined in steel. Isoamyl alcohol was used as solvent. A colorimetric method for the determination of aluminum in the presence of large amounts of beryllium has been worked out by R. V. Mervel (1945). Determination is based on extraction of aluminum hydroxyquinolate from acetic acid solution. Extraction of aluminum hydroxyquinolate has also been studied by M. M. Raines and Yu. A. Larionov (1948).

A. I. Busev (1949), has developed an extraction-colorimetric method for determining osmium in the presence of ruthenium without preliminary separation of these metals.

It was found that the thiourea complex of ruthenium does not interact with diethyldithiophosphoric acid, while the thiourea complex of ruthenium quantitatively reacts with diethyldithiophosphoric acid to form an inner complex compound which is practically completely extracted by organic solvents in one stage. In this method, appreciable amounts of iridium, platinum, gold, iron, and copper do not interfere with osmium determination.

A.I. Busev and M.I. Ivanyutin (1957) have developed an extraction method for determining palladium in the presence of platinum and other elements, in the form of diethyldithiophosphates. Yu.A. Chernikhov and B.M. Dobkina (1949) have carried out a systematic investigation of extraction of elements as their diethyldithiocarbamates, and have suggested procedures for separating a number of elements. A.G. Kovaleva (1952) has studied the extraction of manganese by means of 16 different substituted dithiocarbamates, and improved the extraction-colorimetric determination of this element considerably.

Much work has been carried out on the extraction of other inner complex compounds. Many organic materials containing aromatic nuclei or long aliphatic hydrocarbon chains are suitable as reagents. It was found to be essential that the molecules of the cyclic salts formed by these reagents did not contain hydrophilic groups. Consequently, as V. I. Kuznetsov has pointed out (1954), reagents which contain such isolated groups as SO_3H, $-OH$, and $-COOH$, instead of groups which can interact with the metal ions, are not suitable for extraction.

F. G. Zharovsky (1951) has made a systematic study of the extraction of cupferronates by various solvents.

A series of researches has been devoted to the study of the extraction of dithizonates, which are widely used in analysis for the separation and photometric determination of small amounts of elements of the sulfide group.

A. K. Babko and A. T. Pilipenko (1946), have studied the distribution of dithizone between an aqueous phase and carbon tetrachloride when the pH value of the aqueous phase was altered. During this work the equilibrium constant was determined and it was shown that dithizone behaves like a monobasic acid. For the aqueous phase the concentration of the dithizone anions which form complexes with the metals, can be calculated from the equilibrium concentrations of dithizone molecules in carbon tetrachloride and the value of the pH of the aqueous phase.

A. T. Pilipenko (1950) has studied the composition of the dithizonates of thallium and indium by the method of physicochemical analysis. V. G. Goyushina and E. Ya. Gailis (1953, 1956) have used dithizone for determination of small amounts of gold and silver. In order to eliminate interference from large amounts of copper, bismuth, and lead during determination of silver, Complexone III was added.

I. B. Suprunovich and D. L. Shamshin (1946) showed that the analog of dithizone–ditolylthiocarbazone, forms colored inner complex compounds insoluble in water and readily soluble in carbon tetrachloride and chloroform, with heavy metals; these colored compounds differ from dithizonates by their deeper color and a greater stability towards oxidizing agents.

A. S. Grzhegorzhevsky (1956) has used a solution of di-β-naphthyl-thiocarbazone for extracting nickel and cobalt.

I. M. Korenman and F. R. Sheyanova (1956) have discussed a series of questions related to extraction as a method of physicochemical analysis.

Extraction of Uranium, Thorium, and Transuranium Elements

Russian research workers have carried out a large amount of work on the extraction of uranium, thorium, and transuranium elements. The highly selective extraction of uranyl nitrate by diethyl ether and other oxygen-containing solvents is of widespread analytical application for separating uranium from other elements. It has been found that diethyl ether (which is rather hazardous, due to the risk of fire) can be replaced by a safer mixture consisting of methyl ethyl ketone and carbon tetrachloride (1:2) (V. I. Kuznetsov, 1955).

V. V. Fomin and E. P. Maiorova (1956), have studied complex formation both of indicator as well as quantitative amounts of thorium during extraction of thorium by tributylphosphate from nitric acid solutions with ionic strength 2. It has been shown that the thorium is extracted in tributylphosphate as $Th(NO_3)_4 \cdot 2TBP$, while the partition coefficient of thorium is practically independent of hydrogen ion concentration. It has been calculated that the equilibrium constant of the reaction of complex formation of nitric acid with tributylphosphate is equal to 0.22 ± 0.02, while the equilbrium constant of complex formation of thorium nitrate with TBP is equal to 36 ± 2. By using extraction, the authors have also calculated the instability constants of the complex thorium ions $Th(NO_3)^{3+}$, $Th(NO_3)_2^{2+}$, $Th(NO_3)_3^{+}$ and $Th(NO_3)_4$; they were found to be respectively 6 ±0.5; 13 ± 1; 10 ± 0.5; and 5.5 ± 0.5.

A. M. Rozen (1957) has studied the thermodynamics of extraction with tributylphosphate.

V. M. Vdovenko, A. A. Lipovsky, and M. G. Kuzina (1957), have studied the formation of a complex compound of uranyl in acetone during the use of the nitrate salts of aniline and pyridine as donors of NO_3^- groups. Using a spectrophotometric method, the composition of the complex compound was determined, as well as the constant characterizing its stability. A new compound of pyridine nitrate and uranyl nitrate was isolated and analyzed.

When the acidity is high enough, oxygen-containing solvents are capable of extracting uranium according to an oxonium mechanism.

In the work of V. M. Vdovenko, A. A. Lipovsky, and M. G. Kuzina (1957), it has been shown that formation of the anionic complex $[UO_2(NO_3)_3]^-$ favors extraction of uranium into the ether. A study of the absorption spectra of ethereal solutions shows that the increase in partition coefficients with increasing nitric acid concentration can be basically explained by the formation of similar complexes. It has been suggested that it is not the acids themselves which are extracted, but their oxonium salts which increase the stability of the complex and improve the solubility in the organic solvent.

It is interesting to note that during distribution of nitric acid between aqueous solutions and ether, V. M. Vdovenko and T. V. Kovaleva (1955) observed similar qualitative relationships to those observed during distribution of small amounts of uranyl nitrate.

Much work has been devoted to a study of salting out, without the use of which, normal oxygen containing solvents such as diethyl ether, or ketones, will not extract uranyl nitrate.

In summarizing published results, V. I. Kuznetsov (1954) has observed that nitrates which crystallize out with water of crystallization are particularly good for salting out. Consequently, the nitrates of calcium, aluminum, and iron are better for salting out than the nitrates of ammonia or potassium, for example.

V. M. Vdovenko and T. B. Kovaleva (1955), while studying the distribution of small amounts of uranyl nitrate (about 0.001 molar part) between aqueous solution and ether, in the presence of various nitrates—those of lithium, sodium, potassium, ammonia, mangesium, calcium, strontium, barium, zinc, cadmium, aluminum, and iron— showed that the efficiency of the salting out effect of these nitrates depends not only on the nitrate ion concentration, but also on the cation introduced into the solution. For equal molar parts salted out in the aqueous phase, the salting out effect of the nitrates increases with increasing charge and decreasing radius of the cation. The salting out effect is a consequence of the binding of water molecules during hydration of the cation. Nitrate ions added to the solution with the salting out agent, shift the equilibrium of formation of nitrate complexes towards formation of extractable compounds.

S. M. Karpacheva, L. P. Khorkhorina, and G. D. Agashkina (1957) who have also been concerned with the comparative characteristics of the salting out effect of various nitrates, tested the equilibrium distribution of uranyl nitrate between three extractants (diethyl and dibutyl ethers, and n-butyl acetate). These authors have introduced the concept of the salting out equivalent. This salting out equivalent characterizes the amount of a salt required to salt out one mole of uranyl nitrate in an equilbrium aqueous solution.

I. E. Starik, A. P. Ratner, M. A. Pasvik, and F. L. Ginsburg (1951) during determination of the ratio of plutonium to uranium in a uranium ore, used ethereal extraction for purification of plutonium and uranium from impurities.

I. E. Starik and M. M. Shats (1956), during determination of uranium in stone and iron meteorites, separated it from large amounts of iron by extraction.

A. P. Vinogradov (P. N. Palei, A. K. Lavrukhina, Yu. B. Gerlit, V. A. Khalkin, et al., 1957) has contributed a great deal to the development of extraction processes for separating the far transuranium elements.

Extraction methods are widely used in radiochemistry for separating radioactive isotopes. The chemistry of extraction processes, is probably, identical in principle, both in the case of extraction of macro amounts of material as for distribution of only indicator amounts of the material. Nevertheless, published results relating to the value of partition coefficients for macro concentrations of a given element, cannot be directly applied to extraction of indicator amounts of the same element. The presence of impurities in solution may have a strong influence on the distribution of an element between the aqueous and organic phases. During extraction of radioactive isotopes difficulties may be encountered which are characteristic of radiochemistry, for example, adsorption on glass, formation of radio colloids, etc.

RADIOMETRIC METHODS

V. I. Baranov

Sixty years have elapsed since the discovery of radioactivity (A. Becquerel, 1896). In that time this specialized and initially rather narrow field of science has become one of the foremost in natural science. The present article does not attempt to give a review of those important achievements of the science of matter, which have been obtained during studies of radiations and the transformations of radioactive materials. We shall simply concentrate on the development of methods within the USSR of studying radioactivity, which are most widely used both in analytical chemistry, and in the most diverse scientific and technical fields.

Since it is not possible within the scope of the present article to dwell in detail on all the instances of the application of radiometric methods, we shall confine ourselves to giving an indication of the most important theoretical and practical research work carried out in the USSR on the application of radiometric methods in geology and analytical chemistry.

Methods of Prospecting for Radioactive Ores and Determination of the Contents of Radioelements in Ores and Minerals in Natural Deposits. The first attempt at prospecting for radium deposits by measuring ionization of air was made by A. P. Snesarev (1914) in the Fergansky valley, where several uranium-containing ores were found.

Nevertheless, the real beginning of planned development of field radiometry as one of the methods of applied geophysics dates from the work of L. N. Bogoyavlensky (1922) in the "Belokurikha" resort; he used the method of measuring the intensity of radioactive radiation at various points of the earth's surface, with subsequent plotting on a plan – a "radiometric survey" as he called it.

For his radiometric survey, L. N. Bogoyavlensky used a gamma-electrometer of special construction called a "radiometer." In subsequent field work improved Kolgerster apparatus, employed for measuring cosmic rays, was used for counting the gamma rays, as well as specially constructed field gamma-electrometers.

Field gamma-electrometers have been used not only for prospecting for ores and rocks with a high radioactivity, but also for determining the average content of radium in ores (G. O. Erchikovsky, et al., 1924).

The main advantages of the wide application of field gamma methods for measuring the radioactivity of outcrops during ore working and in quarries have been obvious from the beginning. An important extension of the use of the gamma method was the suggestion made by G. V. Gorshkov and L. M. Kurbatov of measuring the radioactivity of rocks by means of apparatus lowered into bore holes (1935).

The large dimensions of gamma-electrometers, the low efficiency, and the impossibility of counting the apparatus readings at a distance strongly limited the scale and scope of application of the field gamma method.

The new demands placed on the uranium and thorium industry since the second war, have had a great effect on the development of the technics of radiometric work. The turbulent development of research on the physics of the atomic nucleus, accompanied by the creation of various types of construction of measuring apparatus, have enabled a whole series of new techniques to be used in radiometry leading to an increase in the quality and efficiency of work. Mention must first be made of the use of impulse techniques, which have replaced in many instances, the ionization chambers and electrometers used formerly. The use of gas-discharge counters has completed a full revolution in prospecting for radioactive ores. During the post-war years, field gamma-counters were turned out for geological prospecting work. (V. A. Shpak, and G. R. Golbek, 1945). The use of highly sensitive impulse apparatus has led to the extension of the use of gamma-methods for geological purposes, and, in addition to portable gamma-counters, gamma counters have been used with automobile and airplanes (G. S. Smirnov, 1946) and also for ore mining. The theory of the quantitative interpretation of gamma-core sampling diagrams, the determination of the power of ore plasts and their percentage content of radioactive elements (A. P. Kazansky) have been developed in the Institutes of the Ministry of Geology and by the Academy of Sciences. Results of determinations of the amount of ore at an explored deposit by the gamma-core sampling method, gives more accurate results in a number of cases than core testing, particularly when the core yield is incomplete.

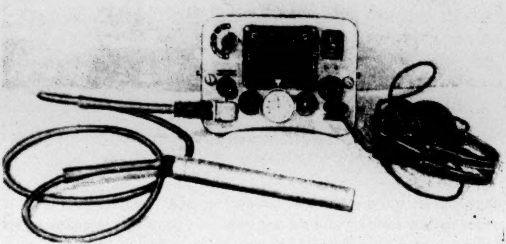
Figure 1. A field gamma-radiometer.

Ore treatment and ore enrichment automatic machines based on measurement of gamma radiation intensity are widely used in practice in many productive organizations.

Mention must also be made of the emanation method of prospecting for ores, which has been used under production conditions by A. P. Kirikov and A. G. Grammakov (1926). Subsequently, the theory of the emanation method was studied in detail by a number of authors (V. I. Baranov, A. G. Grammakov, E. G. Gracheva, and Yu. P. Bulashevich) and has been used in production conditions. The emanation method has been used successfully for looking for ore deposits under a nonradioactive cover which screens the gamma-radiation.

The method suggested by A. G. Grammakov (1946) for isolating the gamma radiation of a definite part of the rock by using a filter screen has found practical application in the radiometric testing of deposits.

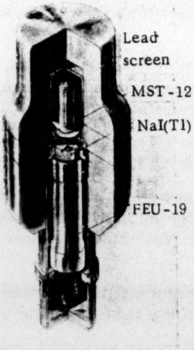

Figure 2. Combined beta and gamma counter.

Laboratory Radiometric Testing of Ores. All control of radium production has been carried out radiometrically by means of the emanation and gamma methods (with partial use of alpha and beta rays).

The characteristic feature of radium as a test object for its radiometric determination is the possibility of determining it quantitatively on the basis of the amount of radon given off; the latter is formed from radium alone, and can be isolated for measurement by purely physical techniques. With increasing development of the methods and techniques of radiometric work, and the increasing demands of industry, radiometry has become an accurate, highly efficient, and inexpensive analytical method.

Radiometric determination of uranium and thorium when both are present together, without chemical separation, is a much more complex problem, and demands the use of special methods of laboratory radiometric analysis of the radioactive raw material. Significant success has been achieved in this field, too (V. I. Baranov, V. L. Shashkin, 1947, and foreign research workers). Combined methods which consists in the meaurement of test samples on the basis of different radiations (alpha, beta, and gamma) with the supplementary use of discrimination according to the various energies, has led to complete substitution of chemical and radiochemical methods by considerably cheaper and more efficient radiometric methods for the separate determination of uranium, thorium, and radium contents of ores when all three elements are present simultaneously.

Such combined methods have also been successfully used not only for evaluating radioactive ores, but for control of technological processing.

Measurement of the Content of Scattered Radioelements. Systematic measurement of the content of radioactive elements in the earth's crust is a very wide field of study.

A technique for measuring the content of radon and thoron in air on the basis of their fission products has been improved by V. I. Baranov (1924); determination of the whole complex of radioisotopes in natural waters was worked out by V. I. Baranov and I. D. Kurbatov (1930); determination of actinium in water was carried out by V. I. Baranov and S. G. Tseitlin (1941); determination of ionium in sea sludge was carried out by L. A. Kuzmina, 1954; while uranium, radium, thorium, and potassium were determined radiometrically in rocks by A. S. Serdyukova, Yu. T. Kapitonov, 1956.

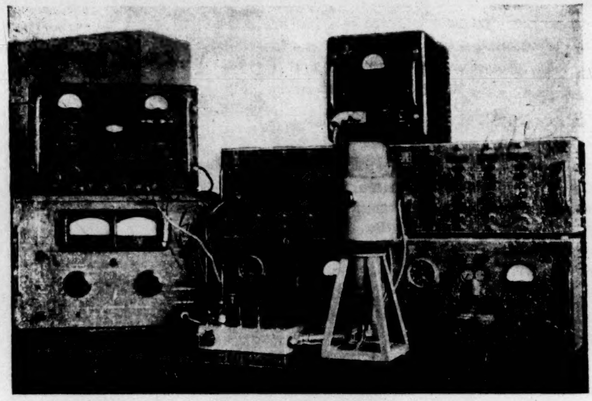

Fig. 3. Combined beta and gamma counter.

Radiometric Methods as Used for the Study of Synthetic Radioisotopes. Many branches of modern science connected with the use of synthetic radioisotopes demand the use of radiometric methods of analysis. Most synthetic radioisotopes are used in small amounts which are beyond the scope of normal analytical methods.

In addition to the most important problem of providing research and industrial organizations with radiometric apparatus (Kozodaev, 1950), it has been necessary to develop special radiometric methods of determining the contents of radioisotopes in complex mixtures.

A setup with multichannel amplitude discrimination (S. A. Baranov, 1953) has been developed for analyzing α-emitting isotopes.

A special problem which has arisen during the study of nuclear reaction products, is the identification of radioisotopes on the basis of their physical parameters (half-life period, nature, and energy of the radiations emitted), and the determination of their absolute yield.

These problems have been successfully solved by the combined effect of workers in the Radium Institute, the Institute of Atomic Energy, and the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci., USSR (1952-1954).

Accuracy of Radiometric Methods. Under the most favorable conditions, for comparing an individual radioisotope with a similar standard (e. g., determination of the amount of radium on the basis of γ-ray measurements) the experimental error can be lowered to 0.1% relative. Determination of the content of β-emitting radioisotopes on an impulse setup in amounts of the order of 1×10^{-7} curies, can be carried out with an error of not more than 5%. At lower contents the error increases to 15%.

The use of scintillation counters has sharply increased the accuracy of measurements based on gamma rays so that it is not less accurate than β-ray measurements. In line with these results, radiometric analysis of complex ores and ores in which radioactive equilibrium has broken down, can be carried out by means of a combined β + γ method, with an error of 5-10%, i.e., with an accuracy which is not less than that of normal industrial chemical analysis.

The sensitivity of radiometric apparatus by means of which it is possible to measure the contents of radioisotopes in solid materials, liquids, and gases, without preliminary enrichment, amounts to 10^{-13} curies/g, for α-emitters and up to 5×10^{-12} curies/g for β- and γ-emitters.

The range of application of radiometric methods is exceptionally wide: from 10^{-13} curies to several dozen and thousands of curies.

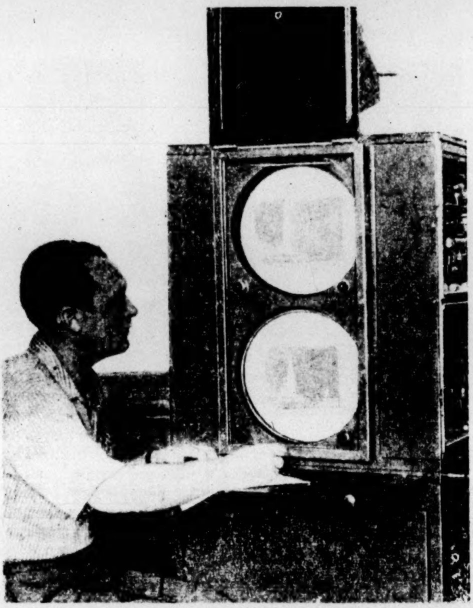

Fig. 4. Multichannel setup for studying the spectra of α-emitters—
V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry.

The Radioautographic Method. The radioautographic method cannot be replaced in two cases: for simultaneously getting photographs of the distribution of a radioisotope over a large surface, e.g., over a plant or animal organ, crystals, etc., (contact radioautography). After developing plates or films exposed for some time in contact with the flat surface of a histological section or the polished section of a mineral sample, there is obtained a detailed image of the distribution of radioisotopes which emit α- or β-rays across the test surface. From the degree of photographic density of the image it is possible, by comparing with standards, to get an approximate evaluation of the concentration of the radioisotopes. This method has found wide application mainly in biology and mineralogy (S. P. Aleksandrov, 1924).

Another variant of the autoradiographic method is so-called microradiography or trace autoradiography, based on the use of special thick layer, so-called nuclear photographic emulsions; on observation under a microscope at a magnification of 500-1000 of the plate which has been developed after exposure, traces of individual α-particles or β-particles in the form of linear little chains of developed silver grains are visible.

In this way it is possible to study the distribution of α-and β-emitting radioisotopes in microscopically small inclusions of rocks or other objects (V. I. Baranov and S. I. Krechmer, 1935).

Radioautography and microradiography are irreplacable during control of the evenness of deposition of a layer of test material or for α-counts on infinitely thin layers.

The microradiographic method can be used for determination of extremely small amounts of α-emitting, long life radioisotopes, since a single α-particle emitted during exposure into the emulsion layer leaves a trace readily detected on observing the plate under a microscope. This method is used in analytical chemistry for example, for determining the amount of α-emitting isotopes of the rare earth elements after irradiation by high-energy particles and chromatographic separation.

From the length of the traces of α-particles in the emulsion, it is possible to identify the radioisotopes which have emitted α-particles of differing energy. In this way it is possible to analyze very small amounts of a material containing radioisotopes; for example, it is possible to determine up to 0.1% of uranium in grains of the order of 0.01 mm.

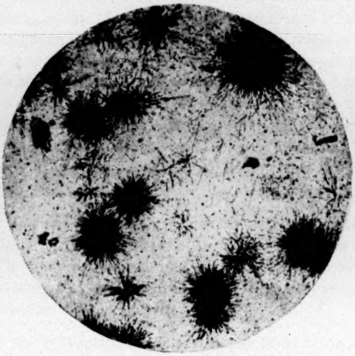

Fig. 5. Microradiography of a mineral (E. I. Zheleznova).

Radiometry is not only a fundamental analytical method for determining the amount of radioisotopes obtained during radioactivation analysis, but can also be used for determining the presence and content of isotopes, which, on being irradiated, enter into nuclear reactions accompanied by expulsion of particles or quanta measured by counters or autoradiographically. As an example we may cite the method worked out in the Curie Institute for determining uranium on the basis of fission fragments by means of microradiography, or the determination of fluorine by counting neutrons expelled during (α, n) reactions.

The vast scale of practical application of atomic energy demands that very serious attention be paid to human health. Accordingly, the dosimetric service is of great importance—this service is the determination of the amount of radioisotopes and the intensity of the radiation emitted by them under conditions where people may come in contact with them, either in the course of their work on atomic energy, or for people in general. Dosimetric control is wholly based on radiometric dosimetric apparatus, which mesures the doses to which people are exposed.

It can be confidently asserted that radiometric methods will assume even more significance in the immediate future in chemical analysis. Automatic machines will be used on an increasing scale. In some cases, nuclear spectroscopy, and the use of new types of counters and special measuring apparatus for combined measurement with multi-channel registration will prove of essential importance.

Many chemical elements can be determined by artificial irradiation of test samples and the measurement of secondary emission.

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ORGANIC REAGENTS

V. I. Kuznetsov

Since the Russian scientists M. A. Ilyinsky and L. A. Chugaev proposed the first synthetic organic reagents for determination of metals –α- nitroso-β- naphthol (1884) and dimethylglyoxime (1905) – the use of organic reagents in analytical chemistry has been intensively developed by many foreign and Russian research workers.

Since the Soviet government came to power whole schools have been organized and have grown up, in Moscow, Odessa, Saratov, Gorky, Kharkov and other towns which have been devoted to looking for, studying, and applying organic analytical reagents. Organic reagents are being successfully used in all branches of analytical chemistry. There is not a single analyst who, at some time or other, has not used organic reagents. Consequently, even those analysts who have not been directly concerned with searching for new organic reagents, have contributed a great deal to developing their application. New organic reagents such a dipicrylamine, chromotrope 2B, thoron, arsenazo (uranon), stilbazo, anthrazo, and others, which were discovered by Soviet analysts are being widely used, not only in Russia, but abroad as well. In the case of other reagents such as methyl violet and amyl acetate, new fields of application have been found for them, so that they are now widely used as reagents.

The use of organic reagents in analytical chemistry is continuously expanding, and their importance is growing. The possibilities of their most expedient further development have been considered in many journals. While there was not even a section devoted to chemical reagents at the All-Union Conference on Analytical Chemistry in 1939, and although the address was approved, in 1956 a special All-Union Conference was held devoted to organic analytical reagents.

Soviet research workers have published a vast amount of work on organic reagents, which occupies an important place in foreign monographs and text books. L. M. Kulberg has written a monograph on "Organic Reagents in Analytical Chemistry" which has been translated into other languages, and "Syntheses of Organic Reagents."

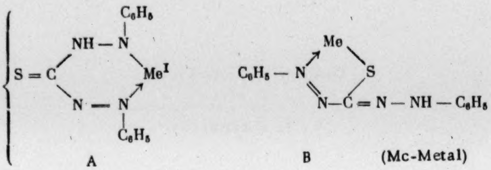
Since it is impossible in this review to cover even the most important fields of application of organic reagents in analytical chemistry, we shall confine ourselves to a compressed outline of their application in only a few branches of analytical chemistry.

Theoretical Research

For an understanding of the fundamental laws governing the behavior of organic reagents and an understanding of the effect of the pH of the medium on them, the so-called hypothesis of analogy (V.I. Kuznetsov, 1947), is important; according to this, reactions of element ions with organic reagents resemble the simplest inorganic reactions of the same ions. Consequently, reactions of reagents of the type R-OH, resemble the reactions of water H-OH, which, in many cases, occur approximately in those regions of pH values in which the ions of the element can be hydrolyzed. Reactions of reagents of the type R-SH are similar to the reactions of hydrogen sulfide, etc.

The analogy hypothesis essentially simplifies an understanding of the effect of pH on the action of organic reagents. Later, this hypothesis was extended to the action of organic ion-exchange materials (V. I. Kuznetsov, 1955), to extraction separation of elements (V. I. Kuznetsov, 1954), and to other cases. Its use for example, led to the detection of the hitherto unknown color reactions of lithium. The analogy hypothesis is useful for getting more accurate formulas for the structures of complex compounds, and in a number of other cases.

Thus, the sulfur containing reagent dithizone only gives color reactions with elements of the hydrogen sulfide and ammonium sulfide groups, as is to be expected on the basis of this hypothesis. It is thus quite incomprehensible why the metal in dithizonates should be represented as being linked to nitrogen and not to sulfur as is often done even at present (A). A careful study of the structure



A B (Mc-Metal)

of dithizonates has convincingly demonstrated that formula (A) is incorrect; the metal is linked to sulfur in dithizonates (B) (G. Irving, S. F. Bell, 1952).

L. A. Chugaev's teaching (1905) regarding the so-called characteristic atomic groups * has been successfully developed by Russian analysts.

The large amount of work carried out by I. M. Korenman (since 1946), L. M. Kulberg (1950), and other research workers has led to the discovery of new groups, which have facilitated the search for new organic reagents and has led to a more accurate understanding of the concept of "characteristic atomic grouping."

A study of the effect of the characteristics of the structure of the molecule of an organic reagent on the properties of the characteristic atomic groups contained in these molecules, has made it possible on these grounds to develop ideas regarding the interaction of organic reagents of differing analytical types. For reagents forming cyclic ("chelate") salts, the mechanism of the interaction with element ions is determined by a characteristic atomic group.

The analytical result – formation of a precipitate or a soluble product, colored or colorless – is often determined by secondary structural characteristics of the reagent molecule. Thus, the presence in a reagent molecule of sulfo groups makes the products formed soluble in water and incapable of being extracted. The absence of sulfo groups has the reverse effect (Fig. 1).

Ideas regarding interactions facilitate the search for new reagents. On the basis of the factual existence for any one element of a valuable reagent of one analytical type, this relationship makes it easy to create a reagent of another analytical type for the same element. Thus, from the very existence of color reactions, it is easy to make reagents for precipitation, coprecipitation, or extraction, of the same elements.

Important results have been obtained in the study of the composition of soluble compounds formed by organic reagents with the ions of elements.

The composition and instability constants of various complex compounds formed with organic reagents have been determined in the work carried out by A. K. Babko, N. P. Komar, and their co-workers and by many other research workers. Stepwise complex formation is almost always observed in the compounds used for colorimetry, they are formed by colored reagents which have a composition of 1:1. The mathematical approach is widely used in N. P. Komar's work.

Another direction taken in the study of the complex compounds formed by organic reagents is the deciphering of the nature of the bonds between the element and the residue of the molecule of the organic reagent. As a consequence of the possibility of the existence of so-called intramolecular dissociation (ionization) in the cyclic compounds formed, in relation to the pH of the medium, the atom of the element in these salts may have either a low or high degree of ionic character. Ideas regarding intramolecular dissociation of cyclic salts has

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* Sometimes they are less accurately called specific atomic groups.

made it possible to understand the effect of pH on the color of the reaction products formed with organic reagents, and their chemical reactivity (V. I. Kuznetsov, 1950).

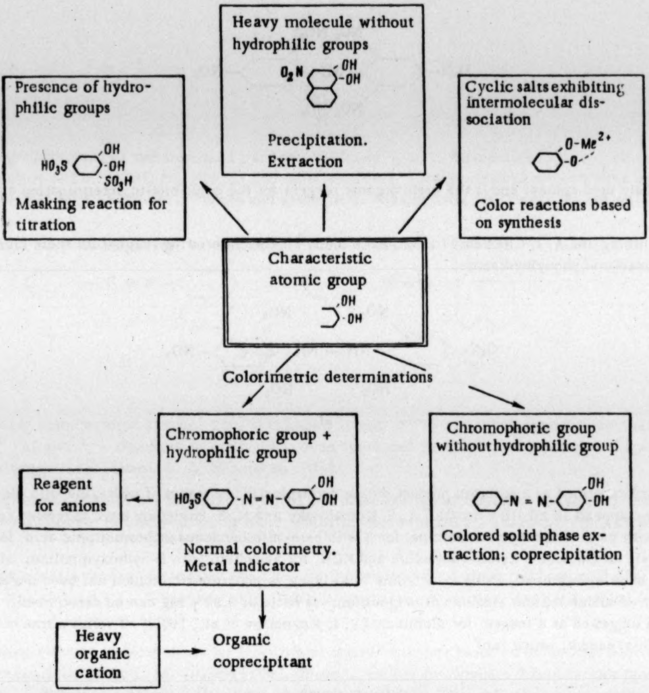

Heavy molecule without hydrophilic groups
O_2N
-OH
-OH
Precipitation. Extraction
Presence of hydrophilic groups
HO_3S
-OH
-OH
SO_3H
Masking reaction for titration
Cyclic salts exhibiting intermolecular dissociation
$O-Me^{2+}$
-O-
Color reactions based on synthesis
Characteristic atomic group
OH
-OH
Colorimetric determinations
Chromophoric group + hydrophilic group
HO_3S
-N = N-
OH
-OH
Normal colorimetry. Metal indicator
Reagent for anions
Chromophoric group without hydrophilic group
-N = N-
OH
-OH
Colored solid phase extraction; coprecipitation
Heavy organic cation
Organic coprecipitant

Fig. 1. Interrelationships between organic reagents of differing analytical types.

A particularly large amount of attention has been given to color reactions. Thanks to the work of V. I. Kuznetsov, L. M. Kulberg, I. M. Korenman, I. S. Mustafin and others on the theory of color reactions, the chromophoric action of the elements, characteristic atomic groups, oxidation-reduction and other reactions, a firm basis has been given to the search for new reagents for color reactions. After carrying out these researches the search for new color reactions for any element does not present any difficulty.

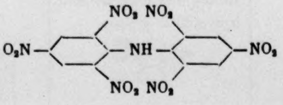
The work which our analysts have carried out on the theory of the action of organic reagents has shown a definite influence on the development of work on organic reagents abroad as well.

Color Reactions and Colorimetric Determinations

Theoretical and practical research on color reactions, and the development of photometric methods of determining the elements have been carried out particularly intensively. Techniques have been developed whereby it is possible in practice to make use of the reactivity of the ions of an element for carrying out color reactions for this element. This makes it possible to have color reactions for practically any cation or anion.

New color reactions have been found and photometric methods developed for the determination of many elements including Li, K, Nb, Ta, quadrivalent lead ($PbCl_6^{2-}$), and for the anions $SnCl_6^{2-}$, $TeCl_6^{2-}$, etc. Many new color reactions have been described for Be, Mg, B, Ge, Al, Sc, Ga, Sb, Tl^{III}, ΣTR, V^{IV}, Cr^{II}, W and for many other elements.

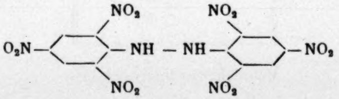
Dipicrylamine (I) which was proposed by N. S. Poluetkov (1933)



I

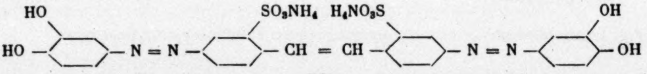
has been widely used abroad, and is the basic organic reagent for the colorimetric determination of these elements.

L. M. Kulberg and A. I. Cherkesov (1952), have found another interesting reagent for these elements; this reagent is hexanitrodiphenylhydrazine.



II

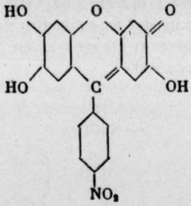
This compound is formed as a reaction product during determination of traces of hydrazine with picrylchloride. A violet color appears in alkaline media. A. S. Komarovsky and N. S. Poluetkov have suggested color reactions for Be with para-nitrobenzeneazoorcine, for B with para-nitrobenzeneazochromotropic acid, for Mo with α,α'-dipyridyl, for Cu with 8-hydroxyquinoline and KCN, for vanadium with 8-hydroxyqinoline; all these reactions have been widely used. Using eriochrome blue-black, a photometric method has been developed for determination of submicrogram amounts of magnesium; as little as 0.05 γ Mg can be determined. Stilbazo (III) has been suggested as a reagent for aluminum (V. I. Kuznetsov et al., 1950); it forms a rose color with the latter; This reagent, which is of



III

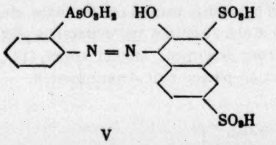
interest for other elements as well, is now produced abroad. For the photometric determination of Ce^{IV} in the presence of other rare earths, use has been made of the yellow color of the nitrate complex of Ce^{IV} in alkaline media (D. I. Ryabchikov). Ce^{IV} gives a very selective color reaction – a blue precipitate – with anthranilic acid (F. M. Shemyakin, A. N. Belokon, 1938).

Using phenylfluorone, a method has been developed for the determination of Ge in ores. After preliminary extraction of Ge as $GeCl_4$, the sensitivity amounts to $10^{-5}\%$ (V. A. Nazarenko, R. V. Ravitskaya, 1956). Substituted trihydroxyfluorones have been recommended for photometric determinations of Sn and Sb. 9-(4-nitrophenyl)-2,3,7-trihydroxy-6-fluorone (IV) has been used for photometric determination of 1–30 γ Sn.

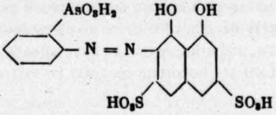


IV

The reagents thoron (V) and arsenazo (uranone) (VI) found by V. I. Kuznetsov (1941) are widely used for determination of Th, Zr, Al, Be, ΣTR, Li and other elements. Foreign research workers have published a large volume of work on the use of thoron and arsenazo for determination of Th, Zr, F, and sulfates.



V



VI

Thoron is being manufactured abroad. Thoron is known abroad as "Thoron," "Thorine," "Naphtharson," "Thoronol," "APANS." A photometric method has been developed for zirconium in which p-dimethyl aminoazophenylarsonic acid is used (V. A. Nazarenko, 1937).

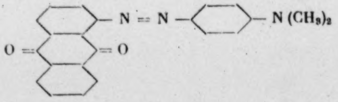
I. B. Suprunovich (1938) has suggested naphthyl and other analogs of dithizone as reagents since they have the advantage over dithizone of being more sensitive. Di-β-naphthylcarbazone ("DN") is recommended abroad.

Many new color reactions have been described for the anions; thiosulfates, sulfites, oxalates, thiocyanates, iodides (A. N. Kreshkov, K. I. Filippova, 1953), sulfates, selenates, phosphates, tungstates, chlorides, bromides, and iodides (V. I. Kuznetsov, 1951).

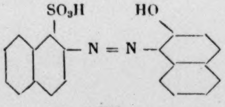
Interesting research work on the color reactions of organic reagents based on oxidation-reduction processes has been published by L. M. Kulberg (1953, et seq.). He has developed a theory for this type of reaction and has found many practical applications for detection of Au^{III}, Tl^{III} and many other oxidizing agents, using benzidene, tolidine, leuco brilliant green, and other reagents. Benzidene and the leuco base of malachite green have already been recommended for detection of iridium ($IrCl_6^{2-}$) (L. A. Chugaev, 1929; V. G. Khlopin, 1926). The indophenol reaction – based on formation of indophenol from aniline and phenol – has proved to be highly specific for elemental chlorine. Bromine, iodine, H_2O_2, salts of Mn^{IV}, mono- and dichloramines do not give the reaction (L. M. Kulberg, L. D. Borzova, 1956).

So-called "colored solid phase reactions" have proved interesting in the case of a number of elements (V. I. Kuznetsov, 1949); their characteristic is that they can be based on simple salt formation, and can accordingly be used for any inorganic cations and anions, including the cations of the alkali metals. They are also applicable to many organic cations and anions. Colored solid phase reactions are particularly important for elements which form characteristic, and stable but not too hydrophilic complex anions, such as $SbCl_6^-$, $CdBr_4^{2-}$, $Zn(SCN)_4^{2-}$, $TeCl_4^-$, $AuCl_4^-$, HgI_4^{2-} and similar ones. Many color reactions for such anions have been described. Tetramethyl diaminodiphenylantipyrylcarbinol salts give a highly contrasting color reaction with zinc; solutions of the reagent are red, while the suspensions of the salt formed ($(C_{28}H_{31}ON_4)_2[Zn(SCN)_4]$ are blue (V. P. Zhivopistsev, 1954). This reaction is analogous to the reaction of zinc with methyl violet (V. I. Kuznetsov, 1947). Photometric determinations of W, Hg, etc., have been developed on the basis of reactions with methyl violet. A colored solid phase reaction for tellurium ($TeCl_6^{2-}$) with the reagent anthrazo enables 0.006γ Te to be detected; tellurium can also be detected with this reagent in the presence of selenium at a ratio of Te:Se of 1:15,000 (V. I. Kuznetsov, 1946).

2-Hydroxynaphthalene-<1-azo-2>naphthalene-1-sulfonic acid (VIII), which gives bright colored solid phase reactions as the pyridine salt, has been recommended for evaluating the amount of mineral salts in distilled water. In absolutely pure water this reagent gives an orange solution, while in water which contains mineral salts a red turbidity develops (V. I. Kuznetsov, 1948).

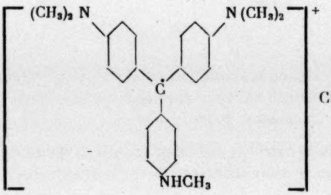


VII

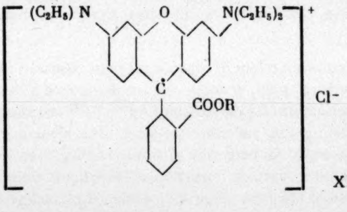


VIII

Since suspensions even of normal salts,[*] formed during colored solid phase reactions can be extracted, photometric determination is possible when a suitable extraction technique is used. At present since it has become clear that extraction-photometric determination can be readily carried out for many elements, this technique is being actively developed both here and abroad. Color reactions and extraction-photometric determination of Sb, Tl, Ta, and other elements have already been described. Methyl violet, (IX), Rhodamine B (X), and Rhodamine 3B (XI) are important reagents for extraction-photometric determination.



IX



X R = —H

XI R = —C_2H_5

Organic Precipitants and Coprecipitants

Soviet analysts have proposed a number of new organic precipitants and have successfully worked on the improvement of methods of using those already known.

Organic reagents which contain in their molecule two or more characteristic atomic groups bind the elements more firmly than reagents of similar structure possessing only one such group (V. I. Kuznetsov, 1955). In the case of a precipitant more complete precipitation is observed. V. M. Dziomko (1953) has illustrated the possibility of improving precipitating capacity taking substituted 8-hydroxyquinolines as examples.

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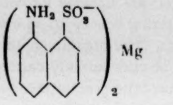
[*] They are sometimes incorrectly termed "complexes."

Dipicrylamine (I) which is used for photometric determination of K, Rb, and Cs, is, at the same time, a precipitant for these elements, and separates them from sodium. Precipitation of potassium as bitartrate can be significantly improved by using aniline bitartrate as reagent (A. F. Ievinsh, Ya. K. Ozol, 1953).

The number of known precipitants for sodium is very small. Accordingly, the new precipitant, magnesium 1,8-aminonaphthalenesulfonate (XII), which precipitates sodium, and, at the same time, separates it from potassium, is of great interest.



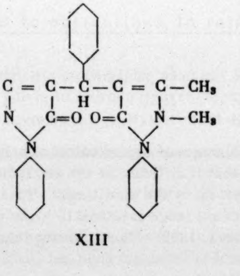
XII

Gravimetric and volumetric determinations are possible with this reagent (R. M. Dranitskaya, 1953).

Phenylarsonic acid has been suggested as a highly selective precipitant for Nb and Ta (I. P. Alimarin and B. I. Frid, 1938). The reasons why results obtained during precipitation of tin with this reagent are not reproducible have been clarified, and it has been shown that phenylarsonic acid is not a suitable reagent for precipitating this element (V. I. Kuznetsov, 1940). Recently, it was discovered that arylarsonic acids can precipitate germanium (K. L. Malyarov, L. S. Kolesnikova, 1955).

Diethyldithiophosphoric acid $(C_2H_5O)_2PSSH$ and its analogs which were suggested by A. I. Busev (1949, 1956), and which precipitate certain elements and give color reactions with them, have proved interesting reagents. Diethyldithiophosphoric acid is applicable to color reactions for Mo, Os; in the form of its nickel salt for the potentiometric and photometric determination of copper; for separating cadmium from zinc and other elements; for determination of lead in the presence of barium, calcium, for the gravimetric, titrimetric and photometric determination of palladium in the presence of platinum and other elements.

Considerable research has been carried out on the precipitation of the heavy anions formed by certain elements using reagents containing heavy organic cations. For example, methyl violet has been used for precipitating zinc ($Zn(SCN)_4^{2-}$ (M. A. Popov, 1947), and antimony ($SbCl_6^-$); Methylene blue for zinc (B. A. Platunov, E. I. Mikhailovskaya, 1953), and tungsten; acridine for zinc (N. A. Filippova, Yu. Yu. Lurye, 1950); brucine and antipyrine for cadmium ($CdBr_4^{2-}$) (I. M. Korenman, 1937; S. I. Busev, 1949); 6- or 8-methylquinaldine for tungsten (R. B. Golubtsova, F. M. Shemyakin, 1951) and many others. Diantipyrylphenylmethane (XIII) forms particularly large, heavy cations, and is capable therefore of precipitating vanadium in the form of $(C_{29}H_{28}O_2N_4)_2 \cdot H_4V_6O_{17}$ from acid solutions.



XIII

Reagents which form lighter cations do not completely precipitate vanadium (S. I. Gusev et al. 1951).

A large amount of work has been carried out by E. A. Ostroumov (since 1947) on hydrolytic precipitation and separation of elements by the use of ashless buffer mixtures based on urotropine, pyridine, and its analogs.

During recent years, V. I. Kuznetsov and co-workers (since 1954) have found a new class of organic reagents—organic coprecipitants. These coprecipitants are suitable for concentrating elements from very dilute solutions; they are capable for example of coprecipitating 0.1-1γ of an element from 1000 ml of solution, and, at the same time, separate it from many other elements. The organic coprecipitant is readily removed from the precipitate obtained by simple ashing; the latter can be conveniently carried out in an automatic oven with a movable hearth (Fig. 2). Because of its organic nature, the precipitates hardly absorb any other elements. The theoretical basis on which a search can be made for organic coprecipitants, and the methods of using such coprecipitants have been worked out, as well as methods for the coprecipitation of In, Tl, and Bi with simultaneous separation from other elements.

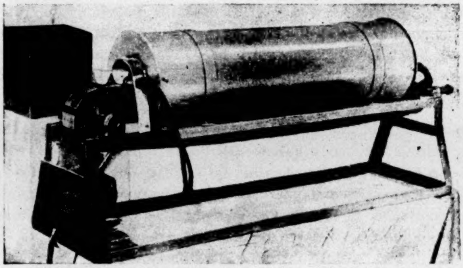


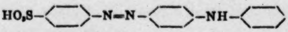
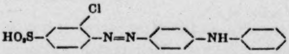
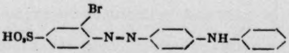
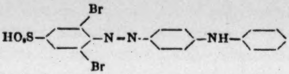
Fig. 2. Oven with movable hearth for automatic ashing of organic precipitates.

The phenomenon of coprecipitation observed during the use of organic reagents has been studied experimentally (I. M. Korenman, 1956). Using coprecipitation of nickel with a precipitate of $Zn[Hg(SCN)_4]$, and using dimethylglyoxime for detecting coprecipitated nickel, it has been found possible to carry out a sensitive reaction for 0.01γ of nickel at a dilution of the nickel of $1:2\times10^6$ (I. M. Korenman, 1938).

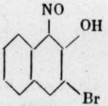
Indicators and Other Fields of Application of Organic Reagents in Inorganic Analysis

pH-Indicators. A monograph has been published on pH-indicators by Yu. V. Karyakin (1951). Some pH-indicators are simultaneously organic reagents capable of giving color reactions. Salt errors of a special kind are characteristic of such pH-indicators (V. I. Kuznetsov, 1950).

The introduction into the molecules of azoindicators of bulky indifferent substituents in the ortho position with respect to the azo group, makes it difficult for the azo indicators to change over into the acid form as a consequence of steric hindrance set up by the substituents. Thus, starting with known azo indicators, it is possible to make analogs in which the pH range is shifted to lower values as compared with the parent substances (V. I. Kuznetsov and G. I. Kosheleva, 1952). The following relationships hold for the indicator tropeolin OO and its analogs:

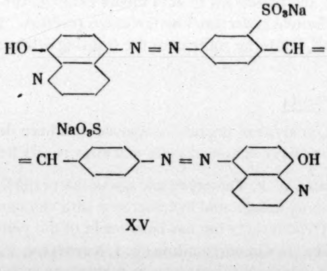
	pK and color change interval
	1.56: pH 1.3—2.6
	0.76
	0.68
	−0.55; from 4 N HCl to 0.8 N HCl

Metal Indicators for Titration with Solutions of Complexing Agents. Of a large number of suggested indicators of various types for mercuro and mercurimetry, 1-nitroso-2-hydroxy-3-bromonaphthalene stands out ("bromonitrozol" XIV); using this indicator it is possible to carry out convenient and accurate mercurimetric determinations of chlorides (L. M. Kulberg, I. S. Mustaphin, 1953).



XIV

As little as 1γ of mercury can be titrated with an error of not more than 1-2%, when the titration is carried out in a special way, and the reagent "stilboxene" XV is used as the indicator (V. I. Kuznetsov, E. B. Mitrofanova, 1956).



XV

Many indicators have been suggested instead of eriochrome-blue-black-T for use during titration with ethylenediaminetetracetate (T. B. Styunkel et al., 1952). Of indicators of the triphenylmethane series, very contrasting color changes −red ↔ green− is given by the indicator Chromoxan Green GG (XVI) (I. S. Mustafin, E. A. Kashkovskaya, 1957); The reagent "Kaltson" *(XVII) has been suggested as a substitute for the unstable murexide during titration of calcium in the presence of magnesium; solutions of Kaltson are completely stable (V. I.

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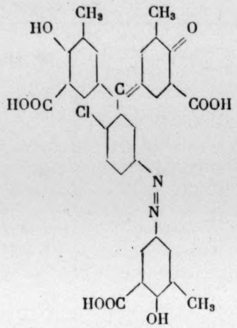
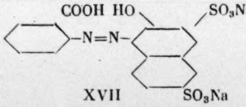
* Transliteration of Russian — Publisher's note.

Kuznetsov, V. A. Mikhailov, 1957). The technique and accuracy are the same as for murexide.



XVI



XVII

Oxidation-Reduction Indicators. Phenylanthranilic acid which was suggested by A. V. Kirsanov and V. M. Cherkasov (1936) has proved to be a very convenient indicator for vanadometric titrations (V. S. Syrokomsky, V. V. Stepin, 1936). This indicator has been essentially responsible for the development of vanadometry.

Microcrystalloscopic Reactions. Organic reagents are often used for carrying out microcrystalloscopic reactions. A review of the most important work in this field is given in a special article (p. 679).

Catalytic Reactions. A catalytic reaction based on the oxidation of aniline by potassium chlorate in the presence of 8-hydroxyquinoline has been suggested for the determination of 0.005-0.5γ of V (V. A. Nazarenko, E. A. Biryuk, 1955). Osmium and ruthenium in acid media catalyze the reduction of nitrate to nitrite by organic compounds. The nitrite formed is detected by the diazo reaction. The limiting dilution for detection of osmium amounts to $1:1 \times 10^{10}$, while for ruthenium the limiting dilution is $1:5 \times 10^{9}$ (V. I. Kuznetsov, 1950).

Analysis of Organic Compounds

Compared to inorganic analysis, analysis of organic compounds has been developed to a considerably less extent. All the same, Russian chemists have achieved some successes in this field too.

Using dinitrophenyldiazonium salts, A. P. Terentyev and co-workers (1937), have developed interesting techniques for detecting and determining unsaturated hydrocarbons with conjugated double bonds. For determination of polychloronaphthalenes ("Halevaks")[*] use has been made of the yellow color of the molecular compounds formed on dissolving Halovaks in dimethylaniline (V. I. Kuznetsov, Z. M. Pimenova, 1951). G. Vanag and E. Vanag (1955) have suggested a selective reaction for formaldehyde with nitroindanedione.

S. I. Burmistrov (1946 et seq.), has described a large number of color reactions for organic compounds, mainly of the aromatic series: amines, phenols, and many others. The numerous examples he has given give an idea of the limitations of the reactions described by him. In some cases, these limitations can be derived from theoretical considerations. The application of the hypothesis of chromophoric action of the elements, and of the intramolecular ionization of cyclic salts, has made it possible to decipher the colors and the effect of pH on the colors which develop during the ferric chloride reaction for phenols. It has also been possible to correct some inaccuracies in the colors reported in the literature (V. I. Kuznetsov, 1956).

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[*] Transliteration of Russian — Publisher's note.

L. M. Kulberg and I. S. Mustafin (1952) use paper soaked with a solution of Malachite Green and subsequently dried, for detection of piperidine as impurity in pyridine. The presence of as little as 0.1% of piperidine leads to decolorization of the Malachite Green. A. P. Kreshkov and co-workers (1954), have carried out a great deal of work on the analysis of organosilicon compounds. Color reactions of substituted silanes with Michler's ketone have been worked out.

The examples given in this article by no means indicate the scale of work of Soviet analysts on the use of organic reagents in all branches of analytical chemistry. Organic reagents are being successfully used in all branches, and Soviet analysts are contributing their share to their development.

It should be mentioned that some branches of analytical chemistry such as extraction separation of the elements, complexometry (titration with solutions of ethylenediaminetetracetate), ascorbinometry, chloraminometry, mercuroreductometry, are wholly based on the use of organic reagents. Organic ion-exchange materials are really organic reagents. In many other fields— vanadometry, cerimetry, permanganatometry – organic reagents are also used. Organic reagents are of great importance in polarography, amperometric titration, and radiometric methods of analysis. Organic reagents are used for preliminary concentration of elements during spectrographic, polarographic, and various other determinations.

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SPECTROGRAPHIC ANALYSIS

S. M. Raisky

Almost seventy years passed after the discovery of emission spectral analysis (Kirchoff and Bunsen, 1860) before it found its first practical application in industry. The great importance of this method in the field of scientific research (discovery of new elements; study of the composition of the heavenly bodies; diciphering the nature of α-particles emitted by natural radioactive isotopes) has led to numerous attempts to use spectral analysis for solving practical problems. Nevertheless, all these attempts were unsuccessful since the level of knowledge of the structure of the atom and the laws of emission of light was insufficient to establish a well-defined connection between the chemical composition of a test sample and its characteristic spectra. Only modern quantum mechanics was able to throw some light on the nature of the difficulties standing in the way of quantitative spectrographic analysis. The study of homologous lines and the principles of measuring intensity by comparing the spectrum lines of impurities with the homologous lines in the spectra of the base element (Gerlach, 1926) created the requisite scientific basis for quantitative spectrographic analysis. Since that time the method has been developed reliably and rapidly.

In the Soviet Union the first papers on the practical application of the method were published by A. N. Filippov (State Optical Institute), S. A. Borovik (The V. I. Vernadsky Laboratory of Geochemistry), and A. K. Rusanov (All-Union Institute of Mineral Raw Materials). The work described in these papers, and which was carried out towards the end of the twenties and the beginning of the thirties of the present century, was devoted to the analysis of ores and minerals, test objects which showed up clearly the basic advantage of the method– its high sensitivity– while at the same time played down the rather weaker side of the first quantitative experiments– the rather low accuracy of the results. In 1931 G. S. Landsberg, co-workers, and pupils started systematic development of practical spectrographic analysis. The objects of investigation were chosen from a number of problems which were interesting a large industrial enterprise– the Moscow Automobile Factory AMO (nowadays, The Likhachev Auto Factory-ZIL). In 1935 a solution was found for some exceedingly important questions, namely, rapid sorting (1-2 minutes) of types of alloyed steel, and express analysis of steel for the elements used for making the alloys (determination of each element took 5-6 minutes, experimental error was ± 5-7% relative). The construction of simple, specialized setups, in which visual methods of carrying out photometric determinations were used (styloscope and stylometer) made it possible in a very short space of time to extend the experience in the auto factory to other enterprises. In the Soviet Union—in the course of a few months, with one styloscope operating round the clock, hundreds of thousands of determinations were carried out, and it was possible to liquidate the backlog of sorting out the metals, a problem which had been holding up normal production of automobiles, This apparatus which has been modernized and produced in its thousands still maintains its importance at present.

The principles employed in solving the problem of sorting out steel according to its mark, and the express analysis of steel, have served as a basis for subsequent diverse applications of the styloscope and stylometer: for sorting out nonferrous metals; control of smelting of steel and nonferrous metals; control of the chemical composition of details, intermediates, and finished articles (without damage to them).

Methodological developments carried out by a large number of spectroscopists and analysts, and the experience gained in many dozens of enterprises were systematized in 1940 in a special monograph. Visual methods of spectrographic analysis had by this time found a firm position in the practice of factory laboratories. Together with the advantage of this method–speed of analysis– the limiting accuracy of the method also became more and more evident; the latter preventing the solution of many important problems, such as analysis of the mark of materials for issuing as standards; determination of small concentrations of impurities; determination of elements whose sensitive spectral lines lie in the ultraviolet; analysis of nonconductors and brittle samples (ores, minerals, etc.). The necessity arose therefore of concentrating attention on developing photographic methods of spectral analysis. Though, during the first years, this was hindered by the fact that no spectrographs were being made in the Soviet Union, nevertheless using imported apparatus the ground was layed for the introduction of the more accurate methods of photographic analysis. The working out of the scientific basis for quantitative analysis led to the construction of special arc and spark sources of light distinguished by enhanced stability, and favorable spectral properties; such sources were subsequently issued in their thousands by the optico-mechanical industry. Further, simplified techniques were worked out for measuring the blackening of spectral lines, whereby it was possible to use spectrographs without special microphotometers— production of which came later. As a result, the accuracy of spectrographic methods increased (the error dropped to ± 3-5%) relative, while their field of application increased. The method was introduced into many hundreds of enterprises and became the basic method for controlling the chemical composition of materials. The importance of spectrographic analysis increased further after organizing (since 1945) the mass production of spectrographs, microphotometers, spectroprojectors, spectral plates, etc. The excellent quality of Russian spectrographs is noteworthy, these are: the quartz spectrograph, the ISP-22 or SP-28; the glass spectrograph, the ISP-51, with many variants of linear dispersion and light strength; the quartz-glass autocollimating spectrograph the KS-55 or KSA-1. Our spark and arc sources of light, the IG-2 and DG-1 are also of high quality, as well as the MF-2 microphotometer and the registering microphotometer the MF-4, and the PC-18 and double DSP-1 spectroprojector. The construction and production of spectral apparatus is mainly the result of the work of the LOMZ factory, the State Optical Institute, the Commission of Spectroscopy of the USSR Academy of Sciences, and a large collective of co-workers in other institutions, whose work along these lines in the last 20 years has been brought together by Academician G. S. Landsberg who died so untimely. Thanks to the mass production of apparatus, spectrographic methods have become the basic method of controlling the production of ferrous metals (steel, cast, ferroalloys, scrap, etc.) of nonferrous metals (aluminum, copper, magnesium, nickel, cobalt, tungsten, molybdenum, titanium, niobium, tantalum, uranium, thorium, vanadium, etc.), of articles made by the machine construction industry (automobiles, tractors, airplanes, lathes, etc.), of the ship building industry, of railway transport, of apparatus construction, electro-vacuum construction, etc. Within the framework of this short article it is not possible to enumerate the industrial materials analyzed by spectrographic methods, and to list the elements determined in such materials.

The number of articles published in the Soviet Union during the last 25 years, on spectrographic analysis, amounts to 2000.

Spectrographic methods play an important part in the search for ores and minerals, and also for control during their enrichment and processing. Due to its speed, universality, ease of operation, and cheapness, spectrographic analysis is rapidly becoming of primary importance. All geological administrations, prospecting parties, and scientific-research institutes are provided with spectrographic apparatus, by means of which it is possible to solve the problems of qualitative and quantitative analysis of ores. In the course of the year millions of analyses are carried out in the USSR on samples for their contents of 6-12 elements. These analyses have served for explaining the distribution of elements in outcrops of ore bodies, in which the contents of the elements being determined do not exceed 0.01-0.001%. Using the method of metallometric photographs, parts with high contents of one element or another have been discovered. The study of discovered ores, minerals, and ores requires semiquantitative determination ($^1/_3$ of the order of the expected value) of 45-50 elements, including impurities in amounts of thousandths part of a percent, and, in some cases even smaller amounts. Quantitative spectrographic analysis of mineral test samples is also used in geology (with an error of ± 5-10%). The special features of test samples (complex composition and variable bulk composition, poor electrical conductivity, mechanical properties of the test samples) have necessitated the development of specific methods of quantitative analysis. As a result of systematic studies, simple but moderately accurate methods of analysis (packing the test sample into the crater of a carbon electrode in the arc, strewing the powder through an arc discharge, etc.) as well as methods which took a long time to carry out (analysis of solutions, etc.,) have been replaced by much more improved methods, possessing high sensitivity, high accuracy, and possibility of universal application (the method of blowing powdered test samples through a stabilized flame of an arc discharge — Fig. 1).

Among the finest achievements of Russian spectrographic analysis, mention must also be made of the development of an analytical technique for establishing the content of impurities in particularly pure materials. Special methods have been developed whereby it has been possible to determine 10^{-3}- 10^{-4}% of impurities in tungsten, molybdenum, nickel, copper, cobalt, and other materials. The relative experimental error of such a method lies within the limits of 5-15% relative.

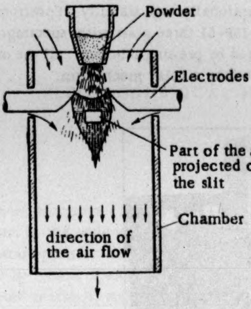
Powder
Electrodes
Part of the arc projected on the slit
Chamber
direction of the air flow

Fig. 1. Schematic diagram of the setup used for analyzing ores by blowing powdered ore into the flame.

Approximately 10 years ago there were developed in the USSR the most advanced new methods of analysis of pure materials; these methods which were known in principle are based on removal of impurities by evaporation, with subsequent excitation of their spectra (Fig. 2). In this way it was found possible to achieve high sensitivities for determination of impurities in thorium, uranium, beryllium, tungsten, and aluminum; in certain instances of the order of 10^{-6}% the experimental error was of the order of 15-20% relative.

The continuously growing demands of production have, in many cases, posed insoluble problems before visual and photographic methods of analysis. Rapid methods of metal production (oxygen blasts), the addition of small amounts of alloying materials, automation of technological processes of metal smelting, and enrichment of ores – all these achievements of modern techniques demand speeding up of analysis to 1-2 minutes, cutting down errors to 1-2% relative, and extending the range of concentrations for which impurities can be analyzed during series analysis from a few dozen percent to 0.001-0.0001%.

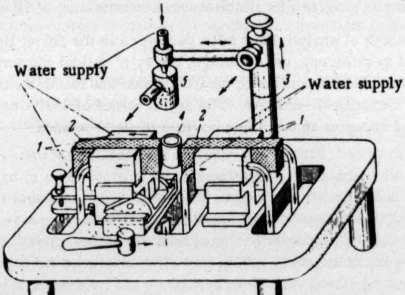

Fig. 2. Evaporating setup: 1) holder for graphite brushes 2; 3) stand with holder 5 for condensate receiver; 4) vessel plus test sample.

These problems can only be solved by using photoelectric methods of spectrographic analysis. Unfortunately, in this respect we are lagging behind some other countries. All the same, at present, considerable effort is being devoted to creating Russian photoelectric setups. The first apparatus suitable for industrial application was produced in 1953.

In 1956 the FES-1 "photoelectric stylometer" (Fig. 3) operating in the visible part of the spectrum was brought into series production. The apparatus which has been developed in the Laboratory of the Commission on Spectroscopy of the USSR Academy of Sciences, makes it possible to carry out successive determinations of elements with an error of ± 0.5-2%; determination of one element takes 1 minute. The light source is an arc with electronic control of the firing of the arc, and possesses exceptionally high stability. Spectrum line intensity is measured by means of a photoelectronic multiplier. The ISP-51 three glass prism spectrograph serves as the spectral apparatus. The setup is automatized; it is started by pressing a button; all the other operations of analysis including termination of the analysis are regulated by a relay mechanism.

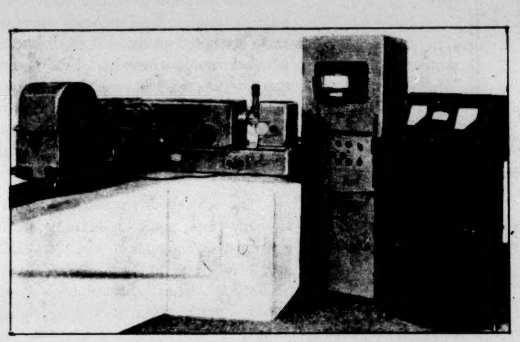

Fig. 3. Photoelectric stylometer FES-1.

At the moment another Russian photoelectric apparatus is undergoing testing; this is the DFS-10 quantometer which has been developed in the State Optical Institute. The apparatus contains 36 channels which makes it possible to compile programs for simultaneous determination of 12 elements in test samples.

Spectrographic methods of analysis have been developed in the Soviet Union on the basis of wide scientific research in the fields of spectroscopy, gas discharge, theory of optical instruments, photographic and photoelectric photometry. This has made it possible to create original and reliable analytical methods which are widely used in all branches of the national economy. The Soviet school of analytical spectroscopists has received general recognition, and occupies an honorable position in world science.

ELECTROCHEMICAL METHODS IN ANALYTICAL CHEMISTRY

M. T. Kozlovsky

The development of analytical chemistry on a wide scale has been characterized during the last thirty or forty years by the wide application of physicochemical methods of analysis. Electrochemical methods occupy an important position among these. The practical importance of many of these methods is determined by the fact that by means of such methods it is possible to determine very small amounts of materials. Some of them are express methods, and, finally, on these are based the overwhelming majority of automatic and telemechanical methods of analysis which have acquired particular significance in recent years, in particular, in connection with the peaceful uses of atomic energy.

The successful development of electrochemical methods of analysis in the USSR has been favored by the fact that Soviet electrochemical science has occupied a leading position in the world in preceding years.

Electrochemical methods of analysis can be subdivided into three main groups:

1) methods in which the amount of material to be determined is established by measuring various electrical values: current strength, quantity of electricity, electrode potentials, electrical conductivity;

2) titrimetric methods of analysis, in which electrical measurements are used for indicating the end point during titration (potentiometric, amperometric, conductometric, high frequency titration, etc.);

3) methods in which the electrical current is used as a reagent in its own right (classical electroanalysis, internal electrolysis, cementation).

At present, some of the methods from the first and second groups are of particular significance. First and foremost of these is polarography – a method based on measurement of the current passing through a circuit during limiting polarization of the electrode.

This method, whose principles were formulated by Ya. Heyrovsky in 1922, has by this time acquired unusually great importance and is used in a variety of ways. Nevertheless, this method did not in fact, penetrate beyond the confines of Heyrovsky's laboratory until after 1933. About that time, studies on polarography were started in the Soviet Union. We owe a great debt of gratitude for the development of polarography in the Soviet Union to V. I. Vernadsky, who, having visited the laboratory of Heyrovsky in 1932, immediately appreciated the value of this method, and sent his co-worker A. P. Vinogradov to Prague to get acquainted with this new method. Soon, on the initiative of E. S. Burkser, the production of the first Soviet polarographs was started in Odessa. At about the same time there appeared the first Soviet work on polarography both from a theoretical and practical point of view.

Theoretical investigations were directed primarily at trying to explain the nature of polarographic maxima (A. N. Frumkin and his school), at explaining the effect of surface active materials on the nature of the polarograms (M. A. Loshkarev, T. A. Kryukova, et al.), at developing a general theory of the diffusion, lying at the foundation of polarography (V. G. Levich), and at a series of other problems. T. A. Kryukova discovered the so-called polarographic maxima of the "second type," gave the theory of these maxima, and showed how it was possible to use them for determining very small amounts of surface active materials.

Most of the work on polarography has been devoted to cathodic processes, since anodic processes on the dropping mercury electrode are restricted by the oxidizability of the mercury itself. A. G. Stromberg and co-workers (1950) carried out significant research on the theory and practice of so-called "amalgam polarography." He pointed out the possibilities of this method for determining small amounts of electronegative metals in the presence of large amounts of the more electropositive metals.

Another feature of work in this field of amalgam polarography was a study of the mutual effect of the metals composing the amalgam; it was established that when intermetallic compounds are formed in the amalgam, a potential shift can be observed both during cathodic deposition of metals on the amalgams, as well as during anodic oxidation of the amalgams (M. T. Kozlovsky and co-workers). This fact, on the one hand, limits the possibilities of amalgam polarography, but, on the other hand, means that it can be utilized for separating metals.

The search for methods of determining small amounts of various metals in the presence of a large excess of more electropositive metals, increasing the sensitivity of the polarographic method, and extending its use to nonaqueous media will be the main lines along which polarography will develop in the future. All these lines of research have been pursued and will continue to be pursued in the Soviet Union.

The first of these problems can be resolved by a purely chemical method – by complexing the appropriate component as a fairly stable complex – or by preliminary separation by electrolysis (P. N. Kovalenko).

Many research workers, in particular I. A. Korshunov, A. G. Stromberg, et al., have been concerned with the study of the effect of various complexing agents during polarographic determinations of various nonferrous metals. Interesting possibilities have been opened up by using complexones.

For detecting small amounts of electronegative metals in the presence of a large amount of more electropositive metals, so-called compensation or "difference polarography," and differential polarography have been used.

Compensation polarography has not yet been used very much by Soviet analysts, and, perhaps has not many possibilities. Differential polarography on the other hand, the bases of which have been worked out by Ya. Heyrovsky, has been developed fairly successfully in the Soviet Union (I. G. Grinman, E. M. Skobets, N. V. Akselrud et al.).

Oscillographic polarography makes it possible to increase the sensitivity of determinations. It must be pointed out, however, that this technique has not yet been studied widely enough in the Soviet Union; the number of papers devoted to this technique is still very small (Ya. P. Gokhshtein, R. Sh. Nigmatullin, I. I. Tsapiv, A. A. Gabovich). This method which has great possibilities, both for studying electrode processes, and for solving practical problems, has however been developed fairly widely abroad.

The polarography of organic compounds has now grown into an independent field. Among many papers mention must be made of the work of M. B. Neiman, I. A. Korshunov, A. L. Markman et al. Since many organic compounds are sparingly soluble in water, the use of polarography for analysis of organic compounds is closely connected with the polarography of nonaqueous solutions, in which N.A. Izmailov's studies have been particularly successful in the Soviet Union.

The polarography of fused media is connected with the substitution of the dropping mercury electrode by solid electrodes. The first attempt at using a platinum electrode in polarography was made as long ago as 1939 by S. D. Miller. Subsequently, research in this field was continued by E. M. Skobets, S. K. Chirkov, Yu. K. Delimarskim, and Yu. S. Lyalikov et al. The latter devoted most attention to the polarography of melts and demonstrated the importance of this method.

In addition to research into the theory of the polarographic method and the development of its variants, a large amount of work has been carried out in the Soviet Union on the practical application of the polarographic method for analysis of ores, metals, and other technical materials. The work of S. A. Pletenev, T. V. Arefyeva, S. I. Sinyakova, Z. S. Mukhina, A. M. Zanko, and P. N. Kovalenko has served as the basis for the wide use of polarography in factory and production laboratories.

During the post-war years, the polarographic method has found use for express, mass, determinations during analysis of mineral raw material (V. G. Sochevanov, D. P. Shcherbov et al.). Worthy of attention is the organization of work on polarographic analysis of ores in the Kazakh Geological Administration (D. P. Shcherbov). In this laboratory, two analysts working in shifts carried out 200 polarographic determinations of nonferrous metals.

Practice in production laboratories has shown that the use of polarographs with photographic registration does not ensure high efficiency, or sufficient accuracy (because of the small size of the galvanometer scale during photographic registration of the current). Consequently, in production laboratories, as a rule, use is now being made of visual polarographs — "polarometers" — in whose construction many research workers have taken part (M. I.Kler, A. G. Stromberg, I. G. Grinman, and co-workers in the State Institute of Nonferrous Metals, Gorky University, The All-Union Institute of Mineral Raw Materials, etc.).

One of the "youngest" electrochemical methods of analysis is coulometry, based on Faraday's law. The Soviet Union, as acknowledged abroad, is the birthplace of coulometry since the founder of this method is M. S. Zakharyevsky, who published in 1938 some work on the coulometric determination of heavy metals in food stuffs. All the same, unfortunately, we must confess that coulonometric methods have not been developed enough in the Soviet Union. This is also true of coulonometric titration proposed in 1938 by the Hungarian chemists, Zsebelledi and Somogi. Of work in the field of coulonometric analysis, there are only a few papers, among which mention should be made of that by F. I. Trishin, who developed an "electrochronometric" method based on measurement of the time necessary for deposition of a metal on a mercury cathode at constant current; and the work of M. T. Kozlovsky, A. I. Lyakh, and A. Zhurhuravleva, devoted to the coulonometric determination of some nonferrous metals at a definite value of the cathode potential, using hydrazine as an anodic depolarizer.

Work started in the field of coulometry by V. S. Syrokomsky was, unfortunately, cut short by the untimely death of the author.

Another technique, which is essentially coulonometric in character, was suggested in 1955 by E. G. Turyan; this consists of reducing organic and inorganic materials on a mercury cathode, and determining the amount of electricity involved by titrating the iodine liberated from potassium iodide on a platinum anode.

The work of A. G. Stromberg on millicoulonometry, and of M. B. Neiman on coulonometric research into the reduction of some organic compounds also belong to the field of coulonometry; their work however is not so much analytical as physicochemical in character.

One must hope that coulonometric methods, in particular, coulonometric titration, will in future attract greater attention from Soviet analysts as methods which enable very small amounts of materials to be determined. In order to develop these methods it is essential that the necessary apparatus be turned out by our industry.

Let us now deal with potentiometric and conductometric methods of analysis.

Direct determination of the concentrations of ions by potentiometric measurements are used mainly for determining pH. During the last 40 years, methods of measuring pH have made a great step forward. Soviet chemists have played an important part in developing the theory of the glass (B. P. Nikolsky, L. I. Belenky, N. A. Izmailov et al.) and antimony electrodes (I. I. Zhukov et al.). A number of new models of tube potentiometers have been constructed, and continuous automatic control of pH has been achieved in many enterprises. Work along these lines continues, the main object being increasing the accuracy of determination.

For determination of hydrogen ion concentration use is also made of conductometric measurements, with the aid of which automatic control of various production solutions has been achieved. Nevertheless, since electrical conductivity is determined by all the ions present in solution, the use of conductometry for analytical purposes is rather restricted. Methods of determining the total content of salts in water and soils have found practical application (S. I. Dolgov, A. A. Shitkov, N. N. Berliner, and N. N. Dolgopolov).

Let us now turn to the use of measurements of electrical values for establishing titration end points. The most important methods in this connection are those of potentiometric and amperometric titration.

Soviet analysts have developed both the theory and practice of potentiometric titration. The most important theoretical work is that of V. S. Syrokomsky and co-workers (mainly Yu. V. Klimenko and V. B. Avilov), devoted to the study of various analytical oxidation-reduction systems, and to explaining the effect of the acidity of the solution and complex formation on the oxidation-reduction potential. V. S. Syrokomsky studied in greatest detail systems formed by vanadium ions of different degrees of oxidation, and worked out a new method of titrimetric analysis – so-called "vanadometry." In our opinion, further study of oxidation-reduction systems can lead to a significant extension of the field of application of titrimetric methods. Thus, not very long ago, S. K. Chirkov used the changes in the value of the oxidation potential of permanganate which occur as a result of changes in the acidity of a solution, for potentiometric titration of mixtures of mineral acids.

In addition to developing the theoretical side of potentiometric titration, a large amount of work has been carried out by Soviet analysts on developing concrete potentiometric methods of determining various materials – primarily, metals. Mention must be made here of the work of A. I. Busev, V. M. Zvenigorodsky, V. G. Sochevanov, S. K. Chirkov, Sh. T. Talipov, D. I. Ryabchikov, N. Ya. Khlopin et al.

Amperometric (polarometric) titration is a branch of polarography. This method which has some outward resemblance to conductometric titration, does however possess some very real advantages over the latter, namely that the presence of other ions does not depress the accuracy of determination, while conductometric titration, as a rule is best carried out in pure solutions. As compared with polarography, amperometric titration is characterized by somewhat greater accuracy, and by the possibility of carrying out determinations of a considerably greater number of ions. Amperometric titration has been widely developed in the Soviet Union, particularly in the post-war years. Approximately one quarter of the articles published on amperometric titration is the work of Soviet authors. To this category belongs the work of I. P. Alimarin and co-workers, work carried out in Dnepropetrovsk (Yu. I. Usatenko, G. E. Bekleshova, G. A. Butenko), in Kazan (A. M. Vasilyev, A. A. Popel, V. F. Toropova, A. N. Marunina), the work of O. A. Songina et al., in Alma Ata, etc. Amperometric titration involving the use of the rotating platinum electrode has been particularly widely used in the work of Soviet analysts. The problem in the immediate future is to apply the proposed methods on a wider scale in practice, and to adapt them for various actual test materials.

High-frequency titration which is a variant of the conductometric method has been attracting the attention of analysts in recent years. This method is based on measurements on the one hand of electrical conductivity, and on the other of the dielectric permeability. The main advantage of this method is the absence of electrodes immersed in the solution, whereby it is possible to work in aggressive media, and to titrate emulsions of various dielectrics. High-frequency titration can be carried out in nonaqueous solutions as well as in aqueous solutions. Systematic work in the field of high-frequency titration has been carried out in the Soviet Union by V. A. Zarinsky and co-workers.

Finally, let us consider electrochemical methods in which the electric current is used as reagent in its own right. As pointed out above, the methods of "classical" electroanalysis, internal electrolysis, and cementation belong to this group.

Of the classical methods of electroanalysis, methods of separating metals from one another when present together in the test material – sometimes in very small amounts – by controlling the cathode potential, have evoked enhanced interest in the last ten years. Although a similar technique was suggested as long ago as 1907, it has only received wide practical use during the last ten years when apparatus became available which enabled the potential to be controlled automatically during electrolysis. In many cases the combination of classical electroanalysis with other electrochemical methods such as polarography, has proved very convenient. Such a "combined" method has been developed successfully by P. N. Kovalenko. At the same time P. N. Kovalenko was occupied with another important question – substitution of platinum electrodes by electrodes made from other metals. In dealing with the use of electroanalysis for separating metals simultaneously present, one must mention the original solution of this question in the case of nickel and cobalt which was suggested by K. A. Nenadkevich and V. S. Saltykova.

The mercury cathode has also been successfully used for separating metals. Work along these lines has been mainly carried out by M. T. Kozlovsky and co-workers. Electrolysis has also been carried out in which the cathode potential is controlled; it was thereby demonstrated that it is possible to use not only cathodic but also anodic processes – electrolytic oxidation of amalgams – for separating metals. For preparing the latter, two methods have been used – either electrolysis with a mercury cathode or replacement (cementation) of the dissolved metal by an amalgam of a more active metal, e.g., zinc or sodium. Both these methods enable metals to be extracted from very dilute solution and subsequently to isolate them from the amalgam by electrolysis with control of the anode potential.

Questions relating to cementation in which amalgams are used have also occupied other research workers, in particular I. V. Tananaev, and Vl. D. Ponoarev, who used the amalgams for quantitative determination and separation of metals, and for brining sparingly soluble precipitates such as lead sulfate into solution. The method of fractional extraction of metals from amalgams proposed by B. A. Tsimmergalk and R. S. Khaimovich is very interesting. This method is essentially a method of cementing, not other metals, but mercury itself; by treating the amalgam with mercury salts and controlling the potential of the amalgam, the research workers mentioned have been able to carry out selective extraction of metals from an amalgam into solution.

Of research in the field of cementation with solid metals, mention must be made of the work of N. A. Tananaev who has studied the cementation of a whole series of metals in various media, using various less noble metals. In his research N. A. Tananaev has shown that the use of the so-called "potential series" for choosing the cementing metal is connected with a number of limitations. Some of the reasons underlying these limitations have been clarified by M. T. Kozlovsky on the basis of the application of polarization curves to cementation theory.

Considerable attention was devoted in the thirties to development of the method of internal electrolysis (Yu. Yu. Lure, Yu. A. Chernikhov, L. B. Ginzburg, M. I. Troitskaya, et al.). This method is a characteristic variant of the cementation process but differs from the latter in that the cathodic and anodic processes are locally restricted, since the displaced metal does not deposit on the cementing metal itself but on a separate cathode. The internal electrolysis method is suitable for extraction of small amounts of certain nonferrous metals.

What has been said above demonstrates how successfully electrochemical methods have been developed in the Soviet Union.

Individual textbooks and monographs have been devoted to electrochemical methods of analysis (S. A. Shchukarev and B. P. Nikolsky, Yu. S. Lyalikov, E. N. Vinogradova, V. A. Pchelin et al.). Monographs by foreign authors have also been published in Russian (Ya. Heyrovsky, I. M. Kolthoff and J. J. Lingane, I. M. Kolthoff and L. A. Laitinen, I. M. Kolthoff and N. G. Fourman, A. Klassen, A. Shleicher and Fischer, et al.). An exhaustive bibliography on the work of Russian authors on electrochemical methods of analysis have been published in the reference book of A. I. Busev on "Analytical Chemistry 1941-1953." It must be pointed out however that publication of literature on electrochemical methods of analysis is still far from being sufficient; this fact, undoubtedly, is one of the hindrances to a fuller introduction of electrochemical methods into the practice of production and factory laboratories.

Another hindrance to the wider practical use of electrochemical methods of analysis is the fact that insufficient modern apparatus is being turned out by our industry.

As a rule, all the valuable studies carried out on electroanalysis, which have issued within our scientific institutions have been carried out on one channel instruments constructed within these institutions.

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PHOTOMETRIC METHODS OF ANALYSIS

V. M. Peshkova and I. I. Antipova-Karataeva

The demands for improved and rapid methods of analysis have led to the rapid development of the colorimetric method which was suggested during the last century by V. M. Severgin, and subsequently led to the development of the spectrophotometric method. Both methods which are based mainly on formation of complexes of the test elements possessing characteristic absorption bands in the infrared, the visible, and ultraviolet regions of the spectrum, have necessitated developments in the theory of the passage of light through the material and in the physicochemical theory of complex formation for their improvement. Apparatus construction has rapidly improved at the same time, and many new Russian colorimeters and spectrophotometers have appeared. All this taken as a whole has led to the wide introduction of photometric methods of study in scientific and production practice.

Development of the Theory of the Interaction of Light with Materials, and the Theory of Complex Compounds

The success of photometric methods of analysis is closely connected with the development of the general theory of the interaction of light with materials, and development of the theory of complex formation. Important work has been carried out in these fields both by Soviet and foreign scientists.

The Ukrainian physicists A. S. Davydov (1951) and S. I. Pekar (1954) have considered the question of the absorption and scattering of light by solutions and crystals. A. S. Davydov (1953) has given a theory for the absorption, dispersion, and scattering of light by solutions. The effect of the solvent on absorption, dispersion, and scattering spectra has been studied. On the assumption that the energy states and the band width are known in the case of free molecules, A. S. Davydov studied the changes which occur when such molecules are in solution. The system molecule – solvent has been investigated. Calculations have been made for a solvent found in the crystalline state, but all the results are justified for the liquid form, as long as the molecule does not succeed in being essentially displaced from the equilibrium position during the phototransition. This is also true for temperatures which are not too high. General formulas have been derived which determine the form of the curves of absorption, scattering, and dispersion of light, and their relationship to temperature and other parameters characterizing the vibrations of the solvent atoms, and their interaction with dissolved molecules in different energy states.

The theoretical ideas of A. S. Davydov and S. I. Pekar have received experimental confirmation in the work carried out in the laboratory directed by A. F. Prikhodko (1954). In addition, a special study was carried out on the temperature relationship of the shape of the absorption bands. In agreement with theory it was found that the absorption bands have a Gaussian form, and their half width is proportional to the square root of the absolute temperature.

Thus, there is at the moment a satisfactory quantum mechanical theory for the interaction of light with a material, which is useful for finding out what happens in the complex processes of absorption of light by complexes.

Development of work on the theory of complex compounds was called for primarily by practical considerations. Colorimetric and spectrophotometric methods of analysis which have found wide application, are based mainly on the formation of complex compounds with characteristic absorption bands. Nevertheless, formation of these compounds and their stability under different conditions have hitherto not been studied in sufficient detail, and analytical techniques have often been based on purely individual empirical observations.

The chemistry of complex compounds is also of great importance for polarographic analysis, for the development of electrolytic methods of separating the metals and for a number of technological question connected with the isolation of rare elements. Nevertheless, there is often no information on the most important characteristics of complexes formed in solution. The photometric method of analysis which is being widely used helps in the study of complex formation; in contrast to the classical preparative method this technique allows one to study complexes directly in solution without their preliminary isolation in a solid form.

The possibility of studying complex compounds by optical methods attracted the attention of Soviet scientists as long ago as the twenties. A. Uspensky and co-workers(1927) succeeded in obtaining results by means of which it was possible to characterize complex compounds of cobalt and chromium on the basis of their absorption spectra, and to study the paths taken by chemical reactions by means of a spectrophotometer. On the basis of the results obtained, a spectrophotometric method was developed for analyzing mixtures of the two components.

During these years the Hungarian scientist A. Kish started to make a systematic study of the absorption spectra of complex compounds, electrolytes, and organic compounds and study the connection between the spectra and the structure of the complexes.

In the experimental and theoretical work carried out on complex formation, most attention was given to objects of interest from the practical point of view – inner complex compounds, and from the theoretical point of view – complexes of the transition elements of the iron group of the rare earth, and of the transuranium elements and platinum group metals. The elements listed, form complexes with characteristic absorption bands, the form, intensity, and position of which in the spectrum is determined by the structure of the complex; these characteristics may, in turn, be used for their identification.

A group of Danish scientists (Kh. K. Jorgensen, S. Zh. Bollhausen, Zh. Bjerrum) carried out a series of theoretical work on the absorption spectra of these elements. They used the results of the classical work of Bethe on the splitting of the atomic terms by the crystal field for developing a theory of absorption of light by complexes found in solution. Energy levels were calculated for a series of complexes of the transition elements from the iron group, and from the actinoids, lanthanides, and platinum metals, and quantitative data were obtained on the positions of the absorption bands in the spectrum which were in fair agreement with experimental results. On the basis of the theory developed, attempts were made to get an idea of the structure of the complexes and of the bonds inside them according to their absorption spectra, L. E. Orgel and a number of other workers have also successfully developed theoretical studies of the absorption spectra of complexes of the transitional elements.

A.V. Babaeva and co-workers (1946, 1956) have studied the effect of the following factors on the absorption spectra of the complex compounds of platinum group metals: 1) the number and positions of the amino groups in the inner sphere of the complex; 2) the nature and number of acid substituents; 3) amido reactions; 4) the charge of the central atom.

Recently a study was made of the complex compounds of the actinoides in solution. N. P. Komar and Z. A. Tretyak (1955) studied complex compounds of the uranyl ion which are of importance in analytical chemistry. The hydrolysis and dissociation constants of the UO_2OH^+ ion were determined. Yu. M. Tolmachev (1944) made a study of the absorption spectra of solutions of thorium salts and thorium complexes. The structure of the carbonate thorium complex has been established, and formation of complex ions in thorium chloride solutions has been studied.

A. K. Babko and a group of co-workers (1945) have been concerned with the theory of complex compounds, in particular with that of inner complex compounds. The most important characteristics of colored materials have been studied in their work, these include: color intensity, which is determined by the coefficient of molar extinction, and the dissociation constant of the colored complex. Considerable attention was given to weakly dissociated complexes – the inner complex compounds – which are so important for photometric methods of analysis. For determining the composition of complex compounds A. K. Babko started to make wide use of the method of isomolar series, which he has described in detail in his monograph "Physicochemical Analysis of Complex Compounds in Solution" (1955). Important results were obtained not only for colored but also for colorless complexes (fluorides). It was shown that it is possible to use physicochemical analysis not only for simple equilibrium between two reacting ions, but also for more complicated systems containing three reacting components.

N.P. Komar and his co-workers (1953) have also been concerned with equilibrium in solution. The method of studying absorption spectra is particularly suitable in the given instance because measurements of the optical density of the solution does not in practice destroy the equilibrium being studied. N. P. Komar showed that is is possible to calculate the following factors for multinuclear complexes: 1) the equilbrium concentration of the components; 2) the integral absorption curve, and 3) to isolate the individual absorption curve for any component in the equilibrium mixture. Foreign scientists have been engaged with similar questions. Of interest among these, in connection with the relation between the absorption spectra of complex compounds and their stability, is the work of R. Williams (1956).

S. A. Shchukarev and O. A. Lobaneva (1955) have made a study of complex formation in solution. They suggested a new combined method of study: the method of Bjerrum's "function formation" combined with measurement of the absorption curves of solutions of known composition. This method enables one to get the distribution of complexes in solution during the process of stepwise complex formation. The absorption bands of individual components can be isolated from the total absorption band, when the maxima of the components in the spectrum are sufficiently separated from each other. The system acetone – $CoBr_2$ and LiBr has been studied.

Of considerable importance from the point of view of spectrophotometric analysis, may be the work which has been started in the USSR on a study of the effect of temperature on absorption spectra (S. V. Gorbachev, P. A. Zagorets, 1955). In addition to getting quantitative results characterizing displacement of absorption bands with increasing temperature, so that it is possible to evaluate the hydration energy of the ions, and to relate it with absorption spectra, it should presumably be possible, in addition, to improve spectrophotometric methods of analyzing multicomponent systems.

One of the most important achievements of Russian scientists is the creation of a number of monographs on complex formation and its relation to absorption spectra (A. K. Babko, N. P. Komar, et. al.), which bring together accumulated experience, and indicate problems to be solved in the future. The most important questions are:

1. The use of physicochemical methods of analysis for studying various groups of compounds which are widely used in chemical analysis or are of importance in theoretical and applied chemistry.

2. The study of chemical interaction between the dissolved material and the solvent.

3. To establish the connection between the stability of complexes and the position of the central ion in the periodic system of elements, and also its connection with other physicochemical characteristics.

By making the correct use of theoretical and experimental results it should be possible in the future to control consciously the processes of formation and decomposition of complexes, and create the basis for making an objective choice between various reagents, and establishing the optimum conditions for carrying out the analysis.

Development of Apparatus Construction

Photocolorimetry started to develop in the USSR in the thirties. All the aparatus which is available can be divided into four types:

1. One arm apparatus with one photo element. The readings of the galvanometer used for measuring the photocurrent, are proportional to the intensity of the light falling on the photoelement.

2. One arm colorimeters with a compensating device having a diaphragam by means of which the galvanometer deviation can be reduced to a given response.

Apparatus of these two types are simple in construction but possess a number of disadvantages. The chief drawback is the need to maintain the voltage in the circuit constant. Furthermore, the accuracy of measurement depends to a large extent on the galvanometer sensitivity and its scale length.

3. Two arm differential colorimeters with two photoelements and an optical compensating photocurrent. Accuracy of measurement does not depend on small voltage variations in the illuminator circuit; nevertheless, it demands careful choice of photoelements which are as near as possible in their characteristics.

4. The most advanced two arm differential colorimeters with one photoelement and with electrical compensation.

Among the first photocolorimeters which found wide use was the apparatus proposed by A. L. Davydov (1936) and B. V. Mikhalchuk (1937) with selenium, potassium, and cuprox photoelements. Subsequently the Gorky State University (1947) issued a series of apparatus: the FOK-45 one arm photocolorimeter, the FOK-D-46 two arm differential photocolorimeter, and the FOK-U-46 universal photocolorimeter, which could be used as a one arm and as a two arm apparatus. The following instruments were constructed in the laboratory of the Scientific Research Institute of Automatics and Control (1947): the DFK-2-0 with a selenium photoelement and an optical logarithmic compensator by means of which it was possible to obtain practically linear calibration curves; the DFK-1-E and DFK-2-E photocolorimeters with electrical compensation. Among later models of interest is V. P. Vendt 's photocolorimeter which has one photoelement the plate of which is cut in two.

In this way two are obtained from one photoelement, and this, to a considerable extent, eliminates the effect of inequalities in the sensitivity of the photoelements, which are observed in apparatus constructed on the basis of a differential scheme with optical compensation.

In the case of the last ten years Soviet industry has issued a number of photocolorimeters. The FEK-M photocolorimeter is constructed on the basis of the scheme of a two arm differential colorimeter with optical compensation. The diaphragms regulating the exposure of the rings are connected to the drums, on which the divisions indicating the optical density of the solution being measured D, and the percentage transmission of the light by solution T are marked. The apparatus is supplied with three light filters with wide transmission ranges and a choice of cuvettes of varying thicknesses, so that is is possible to measure solutions differing appreciably with respect to the intensity of the color without additional dilution.

The photocolorimeter-nephelometers FEK-n-52 and FEK n-54 are also constructed on the basis of a differential scheme. The apparatus has a choice of eleven light filters, one of which has a transmission maximum at 360 mμ. The receiver is an antimony-cesium photoelement which is sensitive to the ultraviolet. Three light filters are available for nephelometric measurements, and, in addition, one neutral filter. By using special attachments the apparatus can be used as a turbidimeter.

In addition to photocolorimeters Soviet industry has also issued two models of the FM diaphragm photometer (Pulfrich type), which differ from each other in the arrangement of the illuminating and photometric parts with the cuvettes. In the first model all the parts are mounted on a horizontal frame, while in the second model the measuring part and cuvettes are arranged vertically, and the illuminating part is fixed at an angle. The light is directed into the vertical part by means of a mirror. Both models are provided with the same choice of filters as the photocolorimeter-nephelometer FEK n-54.

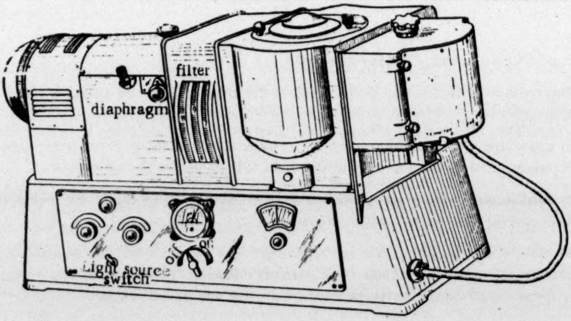

Fig. 1. Simplified spectrophotometer.

At the moment there are available prototypes of the microscope-spectrophotometer designed by N.E. Vedeneeva and V. A. Shamburov (1955) which is no less accurate than the FM photometer, but is free from many of the latter's disadvantages. It is not necessary to work in darkened rooms with this instrument. The absorption curve is traced out by a needle on millimeter paper, so that the eye need not leave the eyepiece and does not become tired. The apparatus contains a rotating wedge shaped disphragm whose displacement is proportional to the density D. The choice of light filters is replaced by a choice of interference light filters. Photometric determinations on luminescent objects are provided for.

During recent years spectrophotometers have started to appear. Many laboratories have at their disposal the SF-4 spectrophotometer – a Beckmann type – which is designed for work in the region 200-1100 mμ. The instrument is a one beam instrument with two interchangeable vacuum photoelements: an antimony-cesium and an oxygen-cesium element. The spectrophotometer has an inclined panel on which all the measuring apparatus is fitted. Such an arrangement of the parts is considerably more convenient for work than the Beckmann spectrophotometer. A simplified spectrophotometer is available nowadays whose measuring apparatus is similar to that of the SF-4, but the prism is replaced by a choice of filters.

The SF-2M spectrophotometer is a two beam instrument which is self registering and is designed for work in the visible at 400-750 mμ. Its dispersion is greater than that of the SF-4, its dispersion part being a double monochromator. Registration of density or percentage transmission is carried out by a pen on paper.

In 1955 a rapid automatic spectrophotometer was constructed at the Institute of Heteroorganic Compounds of the USSR Academy of Sciences. In order to simplify the construction of this instrument and make it cheaper it was constructed on the basis of factory apparatus which is used as a monochromator: the spectograph ISP-22 and the spectrophotometer SF-4. In the first case the receiver was either the photoelements STsV and TsV-3, or the photomultipliers FEU-2 and FEU-20, which are moved by a special mechanism along the spectrum. In the second case the FEU-18 photomultiplier which is fixed securely is used as the receiver. The prism of the spectrophotometer is rotated. The apparatus is a double beam one, the spectrum being registered on the screen of an oscillograph with a high post illumination, so that when necessary the spectra can be photographed on photographic plates. A special photographic attachment is provided. The spectrophotometer makes it possible to register spectra (240-1100 mμ) in 30-60 seconds. The resolving capacity of the spectrophotometer at various recording speeds is: in the visible spectrum 4-2 mμ, in the ultraviolet up to 0.5 mμ. The accuracy of this apparatus is ±1%. The latest model of the apparatus (1956), in contrast to that described, makes it possible to register the density of test materials directly, since for loading the photomultiplier, a diode is used, for which the relation between the current and anode voltage at the beginning of the characteristic is strictly logarithmic. This is a very important advantage of this instrument, since the logarithmic devices – mechanical, potentiometric, and electronic – used before were very complicated.

Thus, during the last 40 years the concerted efforts of workers, on the production side, and scientists have provided a good basis for solving analytical and scientific problems in photometry.

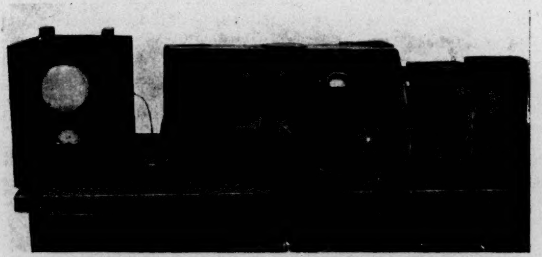

Fig. 2. Rapid self-registering spectrophotometer.

Colorimetric and spectrophotometric methods of analysis are now widely used since they possess high accuracy, they are sensitive and simple. Thousands of papers have been published in Russian and abroad which have been devoted to the determination of individual elements, and the accumulated, rich experimental information has been brought together in monographs.

The results obtained by many Soviet scientists have been brought together in the book by A. K. Babko and A. T. Pilipenko "Colorimetric Analysis" (1951). The monographs of M. Mellon (1950), F. D. Shell and K. T. Shell (1953), and G. Kortyum (1955) are widely known. A collection of articles edited by M. Mellon "Analytical Absorption Spectroscopy, Absorptiometry and Colorimetry" has been translated into Russian and is known to every research worker in this field. The huge number of articles which have been published makes it impossible to deal with them, even with the most interesting ones, consequently we shall confine ourselves to pointing out the most important trends.

During the first years of the industrialization of the country the work of L. A. Chugaevm, V. G. Khlopin, and N. A. Tananaev on control of production appeared. As the individual branches of industry developed, more and more analysts became involved. Thus, S. S. Przhevalsky successfully worked on the analytical chemistry of the industrial production of reagents, I. P. Alimarin worked on the raw materials industry, Yu. A. Chernikov, Yu. Yu. Lurye and S. Yu. Fainberg were occupied with the rare metals and with nonferrous metals, while A. M. Dymov worked on the ferrous metals industry.

Among colorimetric methods of determining trace impurities of elements the most widely used were two visual variants: the method of standard series and colorimetric titration, or "doubling." Standard methods were developed for analyzing ferrous and nonferrous metals and their alloys, and for testing reagents. Simple colorimetric ethods were employed in biochemical and sanitary-hygiene laboratories.

Improvements in colorimetric methods of analysis are closely connected with the discovery of new color reactions. In this field many advances were made thanks to the work of B. I. Kuznetsov, L. M. Kulberg and others, who have discovered a large number of reactions with organic reagents. On the other hand, the possibilities of the photometric method developed with improvements in the apparatus. The switch from visual to photoelectric colorimeters made it possible to extend the spectral region which could be used. It became possible to use reagents giving compounds with certain elements, which absorb not only in the visible but also in the ultraviolet and infrared. Articles have appeared on the analysis of systems the individual components of which form with the same reagent, compounds which absorb in different parts of the spectrum. A. K. Babko and M. M. Korsun (1948) studied the conditions for colorimetric analysis of mixtures of two colored components in the following three cases: 1) during formation of two colored complexes of different metals, or in the case of the presence of another ion possessing a characteristic color; 2) during the use of a reagent with a characteristic color; 3) during formation by a certain ion of two complexes with different coordination numbers and different colors. Work of this type requires preliminary studies of the absorption spectra of the complexes of the test elements. For successful analysis it is necessary to know the region of maximum absorption of the complexes, and either to select appropriate filters for each given multicomponent system, or carry out measurements in these regions on a spectrophotometer (V. M. Chulanovsky, et al., 1948). Before the appearance of spectrophotometers, studies of absorption spectra were carried out in many laboratories on spectrographs. The absorption spectra of test materials, and of standard solutions after multistage attenuation were taken successively on the same photographic plate. The spectra obtained were then measured microphotometrically. A number of methods were suggested for simplifying and speeding up developing of the photographic plates. Thus, V. K. Prokofyev and O. N. Setkin (1944) have suggested a quantitative method of spectrophotometric analysis on a spectrograph without a microphotometer, the accuracy obtained being equivalent to that of photographic photometric measurements.

The use of spectrophotometric methods of analysis has extended the possibilities of chemical methods even further. Thus, N. P. Komar (1950) studied multicomponent systems, and found a method of carrying out spectrophotometric analysis of mixtures of colored materials which tend to dissociate, i.e., for cases where Beer's law is not fulfilled for the system as a whole.

The wide use of colorimetric and spectrophotometric methods of analysis has necessitated careful evaluation of their accuracy. B. V. Mikhalchuk (1945) studied the errors which arise during the use of light filters in photocolorimetry; M. V. Savostyanova (1947), and later K. A. Snesarev (1952) have discussed the errors of spectrophotometric measurements. A study has been made of random and systematic errors.

Infrared spectrometry occupies a special place among spectrophotometric methods of study. Until recently it has been mainly used for analyzing organic compounds and for determining their structure. During the last ten years many papers have appeared, particularly in the foreign literature, which have been devoted to the use of infrared spectrometers for studying minerals. Infrared absorption spectra makes it possible to establish in the structure of the mineral the position of individual groups of elements, e.g., the position of hydroxyl groups, silicate tetrahedra, CO_3^{2-}, O_4^{2-} etc., and also to distinguish between water of crystallization and water of constitution. Attempts have been made to classify minerals. In this connection the work of I. M. Khant, M. P. Vishedr, and L. K. Bonkhan (1950) is of interest; they studied the infrared absorption spectra of more than a hundred inorganic compounds.

Similar studies have started in Russia also. Of interest among published work for example is that of V. A. Florinskaya and R. S. Pechenkina (1956) on the infrared absorption spectra of sodium-silicate glasses, on the basis of which it is possible to establish the spectra of the basic modifications of silica, silicates, and glasses. Some information has been obtained on the structure of glass. E. S. Rudnitskaya (1956) has made a study of the infrared absorption spectra of two types of clay minerals: kaolinite and montmorilite, and has established that it is possible to classify these minerals.

Work on the application of infrared spectrometry for analysis of minerals has been carried out in many scientific centers of the country: in some Institutes of the USSR Academy of Sciences, in the All Union Institute of Mineral Raw Material, in Moscow and Lvov State Universities, and in other establishments.

Thus, spectrophotometric methods of analysis have improved considerably over the last ten years, and are widely used in various branches of science and technics. An important part in the success of spectrophotometry has been played by Soviet scientists, both in the search for new analytical methods for the elements, and in developing the theory of complex compounds and their absorption spectra.

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CHROMATOGRAPHIC ANALYSIS

M. M. Senyavin

The chromatographic method was discovered by M. S. Tsvet as the result of many years of arduous and continuous work on developing a technique for establishing the composition of plant pigments, particularly of chlorophyll. Observation on the incomplete extractability of plant pigments, the assumption regarding the adsorption nature of the phenomenon holding back the pigments, testing of numerous adsorbents, their use in the form of "columns" – these were the most important individual stages of his work, which was started towards the end of the nineteenth century and was brought to completion in the article "A new category of adsorption phenomena and its use in biochemical analysis" (1903) and in an article published in 1906; in these articles, the column of colorless adsorbent with separate colored zones of individual pigments was termed a "chromatogram," while the suggested technique was called "chromatography." These terms have survived until the present day, although it is obvious that their use is arbitrary, for describing separation of colorless materials, in particular of gaseous materials, for experiments on intensely colored – from yellow to black – sorbents, and for experiments in vinyl plastic or metal tubes. The fact that these terms have survived – despite their arbitrary nature – only testifies to the general recognition and the immense importance of the chromatographic method as a dynamic sorption method of separating mixtures for analytical and preparative purposes.

In the development of the work of M. S. Tsvet by Soviet scientists, a large amount of work has been carried out with the object of further improving the chromatographic method, developing its theory, and establishing more accurate conditions for using chromatography for solving a large variety of analytical problems. As a supplement to ion exchange and partition chromatography, T. B. Gapon and E. N. Gapon suggested in 1948 the method of precipitation chromatography, in which separation is based on differences in the solubilities of compounds formed between the components of a test mixture and a "precipitant"; this technique is being used in qualitative and quantitative analysis. Reliable methods of effecting chromatographic separation of gaseous mixtures, which have been called "chromathermographic" and "thermodynamic" were suggested in 1951 by A. A. Zhukhovitsky and N. M. Turkeltaub. The essence of the first technique is a combination of ordinary Tsvet analysis with elution (elution analysis) by moving a heater along the chromatographic column. The advantage of this method is that the zones of the components are constricted in proportion to their displacement along the column, which determines the high degree of chromathermographic separation of mixtures, even of components very similar in properties; in addition, in this case, the zones of all compounds are displaced along the column at the same rate, this being the rate at which the heater is moved; this fact not only cuts down the time necessary to carry out an analysis, as compared with the usual techniques, but makes it possible to identify the components fairly strictly on the basis of the time of their appearance beyond the sorbent layer. The important advantage of the thermodynamic method, in which the heater is rapidly returned to its initial position after completion of one cycle, is the continuity of the experiment.

A significant amount of work by Soviet research workers has been devoted to the theory of chromatography, the first laws of which (adsorption series, ideas regarding adsorption of mixtures, the relationship between the position of the materials in the adsorption series and that on a chromatogram) had already been established by M.S. Tsvet. When N.A. Shilov together with L.K. Lepin and S.A. Voznesensky (1929) showed that the dynamic adsorption process is made up of the period of front formation and the period of parallel displacement of the front. In developing the work of N. A. Shilov, Soviet and foreign research workers not only created the theory of adsorption chromatography, but also demonstrated the applicability of such an approach to partition chromatography (N. A. Fuks, 1948), to dynamic ion exchange processes (N. N. Tunitsky, E. P. Cherneva, V. V. Nekrasov, 1950), and to ion exchange chromatography (N. N. Tunitsky, 1952; O. M. Todesm, V. V. Rachinsky, 1955).

Considerable work has been carried out by Soviet scientists on studying the effect of kinetic factors on the course of a dynamic or chromatographic experiment. M. M. Dubinin (1935) showed that one of the terms in N. A. Shilov's equation – the so-called loss of time of protective action – is kinetic in character, and tends to zero on decreasing the particle size of the sorbent and flow rate of the gas (solution). The theory of sorption dynamics for the case where the rate of the process is determined by external diffusion, was developed by A. A. Zhukhovitsky (1939), who gave a quantitative solution of various problems, and formulated important physical consequences arising from this theory. S. E. Bresler (1955) has given a general though formal solution for the case of inner diffusion kinetics. N. N. Yunitsky and E. P. Cherneva (1953) considered a number of problems in ion exchange chromatography where internal diffusion is the rate determining factor; O. M. Mamontova (1955) has measured the diffusion coefficients of hydrogen and sodium ions on a number of Russian cation exchangers.

While many foreign research workers – usually independently – either develop questions relating to the theory of chromatography, or consider analytical applications of the method, Soviet workers pay considerable attention to establishing the effect of various parameters on the extent of chromatographic separation, and to theoretical prediction of the optimum conditions for carrying out the work. It is obvious that quantitative chromatographic separation of mixtures is achieved in those cases where the distance between zone maxima is greater than the sum of the zone half widths. As A. A. Zhukhovitsky and N. M. Turkeltaub have shown (1956), in the case where longitudinal diffusion is the determining factor, the zone width μ of a component is given by

$$\mu = \sqrt{\frac{mDL}{v}}, \text{ where } m = 4 \ln \frac{c_{max}}{c}; \quad c = c_{max} e^{\frac{x_2 \Gamma}{4DT}}$$

and the distance between the maxima Δx is given by

$$\Delta x = \frac{L \Delta Q}{RT}$$

while the minimum length of the sorbent layer L_{min}, which will ensure quantitative separation is given by

$$L_{min} = \left(\frac{RT}{Q}\right)^2 \frac{mD}{v}.$$

An important physical consequence of these equations is the fact that, in particular, the increase in zone width is proportional to the square root of the length of the sorbent layer (in agreement with the results of N. N. Tunitsky's calculations, 1955), and that the relationship between the distance between the concentration maxima of the zones and the column length is linear.

In developing the theory advanced by Veiss (1943) for the chromatographic displacement of points of given concentration of a material along the sorbent layer

$$vc_i = \frac{v}{\left(\frac{\partial a}{\partial c}\right)_i}$$

A. A. Zhukhovitsky (1955) considered three cases, in two of which (a stationary state and a vertical front) the ratio $(a/c)_i$ enters into the denominator instead of the differential. This means, for example, that for the special case of chromatographic elution of cations by an acid of given concentration, it is possible to forecast on the basis of exchange constants, the moment at which the maximum concentration of a given element will appear beyond the cation exchanger layer.

In order to establish the concentration of the eluting solution in the case where the displacing and displaced ions have different charges, G. V. Samsonov suggested the following criterion:

$$c_{\text{кр}} = mK^{\frac{z_1 z_2}{z_1 - z_2}},$$

according to which, when the displacing ion has the greater charge the zone will be accentuated $C_0 < C_{Cr}$, and vice versa.

As for kinetic factors, then, as follows from the ideas outlined above, one should use a sorbent with the smallest possible particle size, the limit to which they are ground being determined only by the increase in resistance of the layer to the flow of solution. One can also come to a similar conclusion with respect to the effect of the flow rate of the solution on the extent of the chromatographic separation of mixtures. In this case the limit of a rational decrease in the rate is determined by longitudinal diffusion. Nevertheless, special studies on the effect of the flow rate of the solution on the extent of the chromatographic separation, which were carried out by E. P. Shirov and by the present author, led to the following result: the sharpness of zones decreases on increasing the exchange rate (the ratio of the volume of solution passing through in unit time to the volume of sorbent) of the solution flow, but increases, at a given exchange rate, on increasing the rate linearly. Apparently, this result can explain the expediency of turbulent agitation during external diffusion kinetics.

Thanks particularly to the work of Soviet research workers, some success has been achieved in the study of the connection between the sorbability of compounds and their composition and structure. M. M. Dubinin (1947) suggested that it would be expedient to compare the absorbability of a material with its molar volume. On the basis of a consideration of intermolecular interaction between gaseous or dissolved materials and sorbents of different types, M. M. Senyavin showed (1949) that for low values of the occupation of the spaces on the sorbent, the adsorbability of a compound on active charcoal is determined by dispersion forces, and, consequently, on a given sorbent, by the polarizability of the material, while on a polar sorbent of the type of silica gel the dipole moment is also important. In such cases one must also bear in mind both the characteristics of the structure of the molecule (e.g., aromatic compounds are adsorbed better than aliphatics, etc.), and the effect of the structure of the adsorbent. M. M. Dubinin discovered the phenomenon of a decrease in the adsorbability of homologous compounds on a given adsorbent on increasing their molecular weight, this decrease becoming evident at a particular value. This work was subsequently developed into a wide and important field of study on adsorbent structure. The structure of adsorbents has also been studied by A. V. Kiselev and co-workers, and by I. E. Neimark, who established the structural type of silica gel, developed methods for preparing silica gel of uniform pore size, and demonstrated the close relationship between the adsorbability of materials of different structure on the structure of silica gel and the nature of their surfaces. It has been shown that in contrast to adsorption chromatography, in which differences in the adsorbability of materials are shown most clearly on small pore silica gels, in the case of partition chromatography one should take large pore sorbents, as a consequence of lower adsorption capacity and improved kinetics, when internal diffusion determines the rate (N. M. Turkeltaub).

A large number of Soviet scientists have worked on the synthesis of ion-exchange sorbents. F. G. Prokhorov and K. A. Yankovsky have developed methods for preparing sulfo-coal of high quality. Methods of synthesizing cation exchangers have been developed by I. P. Losev, E. B. Trostyanskaya, A. B. Pashkov, A. A. Vansheidt, V. A. Klyachko and many others, while A. B. Davankov, A. B. Pashkov and many others have developed methods for synthesizing anion exchangers. It is sufficient to mention Russian mono- and polyfunctional resins and, condensation, and copolymerization resins such as KU-1, KU-2, SDV, SBS, KB-4, KM, KN, RF, AN-1, AN-4F, N-O, MMG-1, EDE-10 etc. Many Russian ion exchangers are at least as good as the best foreign resins. Of considerable interest at the moment are selective sulfonate cation exchangers whose selectivity is not determined by the nature, or combination of the functional groups, but by their osmotic properties, i.e., by differences which depend on the amount of cross linking agent, and by their capacity to change their volume in water or by the absorption of ions of different sizes (A. B. Pashkov, E. B. Trostyanskaya, 1956).

The importance of Soviet work on the theory of ion exchange chromatography and ion exchange is obvious. In developing the work of Russian soil chemists, particularly the work of K. K. Gedroits (1932), B. P. Nikolsky as long ago as 1934 derived the equation of the constant of ion exchange

$$\frac{a_1^{\frac{1}{z_1}}}{a_2^{\frac{1}{z_2}}} = K\frac{c_1^{\frac{1}{z_1}}}{c_2^{\frac{1}{z_2}}}, \qquad (1)$$

which is still widely used for treating results on the statics of ion exchange. E. N. Gapon on the basis of kinetic ideas, also derived an equation for the exchange isotherm, and put forward a formula for the quantitative calculation of the effect of the acidity of the medium on ion exchange.

During chromatographic separation of a series of mixtures – predominantly mixtures of multicharged ions of similar properties – resort is often made to the use of complexing agents which make it possible to develop more clearly the individuality of one element or another. Many complexes which are also used in chromatographic experiments are being studied intensively in the Soviet Union at the moment in developing fundamental Soviet research on complex compounds. It is sufficient to mention for example the work of A. A. Grinberg, I. V. Tananaev, A. K. Babko and many others on detailed physicochemical studies of the conditions of formation of complexes and their stability. Of interest is the work of D. I. Ryabchikov and E. A. Terentyeva (1949-1952), also that of Ya. A. Fialkev and co-workers (1956), and of A. S. Tikhonov (1954) on the complex compounds of metals with hydroxy acids. In this connection it is important to point out that at the present moment physicochemical methods of analysis (and studies of equilibrium formation of complexes) are being used more and more instead of preparative methods of studying complex compounds.

Nevertheless, despite all this work, a complete quantitative theory of chromatography in the presence of complexing agents has still to be developed. In considering the process of chromatographic separation in the presence of complexing agents, a possible approach may be the suggestion put forward by L. I. Tikhonova and the present author (1956), that the rate of displacement of the zone of a component along a column, in the case of elution by a complexing agent, is determined by the part of the element in the nonsorbed, complexed form. In developing this approach, A. M. Sorochan and M. M. Senyavin (1957) calculated the fraction of lanthanum and ytterbium in the complex form over a wide concentration range in citric acid, and were the first to show quantitatively both the necessity of increasing the pH when using dilute citric acid solutions, and the comparatively greater resolving capacity of one percent solutions of citric acid.

We shall divide the large amount of work carried out by Soviet research workers on the analytical application of chromatography – we can only consider some of this work – into two main divisions: separation of mixtures of organic materials and separation of inorganic materials.

Chromatographic separation of mixtures of organic compounds. As N. M. Turkeltaub has shown (1950), chromatographic separation of mixtures of the lower hydrocarbons is readily achieved by absorption* of the components from a sample of air by means of a column of fine porous charcoal KAD, and then passing pure air through the same column; under the conditions used by the author methane was eluted by 400 ml of air while ethane was eluted by 2000 ml. Individual hydrocarbons from the appropriate fractions were burnt on a platinum wire, the carbon dioxide was absorbed with barium hydroxide and then excess of unreacted reagent titrated. The relative experimental error was 5% for a concentration of test gas in the air of the order of 0.001%.

Separation of gaseous mixtures is considerably more effective when chromathermography is used. A. A. Zhukhovitsky and N. M. Turkeltaub succeeded, by using this method, in separating multicomponent systems of saturated and unsaturated hydrocarbons, containing such components for example as pentane and isopentane, cis-2-butene and trans-2-butene, etc. Chromatographic separation was followed both by means of a gas interferometer and by means of a thermal conductivity cell. A similar method can be used for separating mixtures of inert gases as A. A. Zhukhovitsky and E. V. Vagin (1954) have shown. D. A. Vyakhirev, A. I. Bruk, and S. A. Guglina (1955) followed the chromatographic separation of gaseous mixtures by measuring the volumes of the fractions of the components by means of a nitrogen meter using carbon dioxide as the gas carrier. This technique has been used by the authors for the chromathermographic separation of mixtures of ethane, ethylene, propane, propylene, and butylenes, while N. I. Medvedeva and E. S. Torsueva (1955) used the same technique for the chromathermographic separation of the cracked products of hydrocarbons in order to study the mechanism of this process.

In 1926 B. A. Tarasov developed a method for the sorption determination (on silica gel) of the content of aromatic compounds in various petroleum distillates. In developing his work and also the studies carried out by A. S. Velikovsky (1937), E. A. Mikhailova and B. A. Kazansky (1952), in connection with the development of a combined method for studying the individual composition of straight run distillates, studied in detail the effect of the fundamental parameters of the test method on the extent of the chromatographic separation of aromatic compounds. In carrying out a chromatographic determination of the content of aromatic compounds in benzines, the authors introduced the test mixture onto a silica gel column and then eluted the latter with pentane or isopentane. In order to establish the point at which the aromatic compounds appear in the eluates, the authors introduced a cell with a capacity of 0.1 ml and plane parallel walls between the column and the receiver; when any material which differed in viscosity from the solution passing through the cell previously, passed into this cell, "characteristic striations" readily visible on projecting an image onto a screen by means of a film projector, were observed. On the other hand, in order to make a continuous observation of changes in refractive index of the eluates, the authors used an accurate and universal refractometer based on Fresnel diffraction, constructed by I. V. Obreimov and B. A. Shibalov (1950).

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*Direct translation of Russian — Publisher.

Adsorption chromatography is also being used successfully by Soviet scientists for studying the group composition of high molecular weight petroleum hydrocarbons and their cracked products. The principle of the chromatographic technique developed by S. R. Sergienko and A. A. Mikhnovsky (1955) consists in successive elution from columns of ASK silica gel of the paraffin and naphthenic hydrocarbons, followed by monocyclic, bicyclic, and, finally polycyclic aromatic hydrocarbons, by means of solvents with increasing elution strength: pentane, petroleum ether, benzene, and an alcohol-benzene mixture respectively. A similar chromatographic technique to that described was used by S. R. Sergienko, Yu. A. Bedov, M. P. Teterina, O. I. Delone, and B. E. Davydov (1955) for studying the composition of petroleum resinous materials.

Partition chromatography is also widely used, as well as adsorption chromatography, for separating mixtures of organic compounds, N.A. Fuks and L.S. Chetverikova (1948) have improved a chromatographic method for determining the gamma isomer content of technical hexachlorocyclohexane. The relative error of this method, according to its authors, is 0.2%. V. L. Kretovich, T. V. Drozdova, and I. S. Petrova (1950) developed a technique for the quantitative separation of mixtures of volatile fatty acids by means of partition chromatography. N. M. Turkeltaub (1957) has studied in detail the effect of the structure of the carrier, the nature of the immobile phase, temperature, and other experimental parameters on the extent of the chromatographic separation of mixtures of gaseous hydrocarbons by partition chromatography.

The examples cited above only give an idea of the work of Soviet research workers in the field of separation of mixtures of organic compounds by means of partition chromatography. This method, in addition to its use in organic chemistry, is also widely used in Russia for biochemical investigations; it is sufficient to mention for example the work of T. S. Paskhina, and also that of E. N. Bezinger and O. V. Sdobnikova on amino acids, the work of G. N. Zaitseva, E. K. Surykina, and M. S. Bardinskaya, on carbohydrates, and the work of M. N. Zaprometov on the catechins of tea, and many others. A fairly large proportion of this work has been published in the Transaction of the Conference on Chromatography (1955). We should like to observe that the ultrachemiscope developed by E. S. Brumberg (1950) has proved of great value in following the results of partition chromatography on paper.

For separating mixtures of inorganic compounds the technique most widely used is ion exchange chromatography; partition and precipitation chromatography are used less frequently. The work carried out by Soviet research workers covers the most diverse systems ranging from minerals to nuclear fission products.

Development of effective methods of using chromatography for qualitative purposes is one of the fundamental services rendered by Soviet research workers. K. M. Olshanova and K. V. Chmutov (1953-1956) established so-called "sorption series" on alumina, tentonite, and sulfinite, and pointed out that on this basis it should be possible to separate the elements within the analytical groups normally met in qualitative analysis, and to achieve chromatographic separation of mixtures of cations into groups, which would be based exclusively on the sorbability of the ions. In particular, during chromatographic qualitative analysis of cations on the fourth analytical group, the authors obtained sensitivities of the order of 0.0001 g-equiv/liter, while for lead the sensitivity was 0.01 g-equiv/ liter. An analysis takes 7-8 minutes. A. I. Komlev and L. I. Tsimbalist (1952) demonstrated that precipitation chromatography can be used with advantage in qualitative analysis. In order to detect chloride, bromide, and iodide ions in their mixtures, a few drops of test solution is passed through a dry column of alumina containing silver nitrate or sulfate as precipitant; the limit of identification is of the order of 10 γ. The method of precipitation chromatography on dimethylglyoxime (V. V. Oshchapovsky, 1956) can be used for detecting traces of nickel in the presence of large amounts of cobalt, iron, and copper; the limit of identification for nickel at ratios of nickel to cobalt of 1 : 5,000 is 0.5 γ.

V. D. Kopylova, K. M. Olshanova, and K. V. Chmutov (1956) have studied in detail the relation between the concentration of the test solution of ferric nitrate and the height of the iron zone on a dry column of alumina when potassium ferrocyanide is used as precipitant. In the case studied by the authors almost complete proportionality was observed between the height of the iron zone and its concentration in the original solution, so that, in principle, it should be possible to develop a fairly rapid and simple method for the quantitative determination of some elements.

G. V. Fedorova (1946) has developed a simple sorption technique for determination of sulfates in water; this technique consists in passing the test sample through sulfo-coal in the hydrogen form, followed by titration of the acid eluate thus obtained with alkali; this method was later improved by Yu. M. Kostikin, F. G. Prokhorov, and K. A. Yankovsky (1946-1947). The method suggested by G. V. Fedorova for establishing the titer of alkalis on the basis of sodium chloride or barium chloride is based on the strict equivalence of heterogeneous ion exchange; that this technique is fully satisfactory was demonstrated by Yu. G. Titova (1956). This technique has proved very effective also for the quantitative determination of the content of the salts of organic acids in pharmaceutical preparation (G. A. Vaisman, M. M. Yampolskaya, 1950). As L. M. Orlova has shown (1950) it is possible, in a number of cases, to determine the amount of free acid in salt solutions by the difference between the equivalent concentrations of salt in the original solution, and the acid obtained after passing the test solution through a cation exchanger in the hydrogen form.

Yu. I. Usatenko and O. V. Datsenko (1949) by passing the test solution through a cation exchanger were able to separate phosphate ions during determination of phosphorus in copper phosphide and in ferrophosphorus. A. A. Zanko and Ya. A. Degtyarenko (1952), and also A. I. Laarev (1952) using the same principle, determined boric acid in nickel electrolytes. For the determination of cations of the second and third group in the presence of phosphate ions, Ya. A. Degtyarenko (1952) has recommended passing the test solution through a sulfonate cation exchanger in the hydrogen form, and then desorbing the cations with hydrochloric acid, and determining them in the eluate by normal chemical methods. Yu. V. Morachevsky, M. N. Zvereva, and A. A. Kuznetsova (1956) have suggested an interesting modification of this technique which consists in absorbing the phosphate ions from the test solution, which is decinormal with respect to hydrochloric acid, by means of the anion exchangers PE-9 or EDE-10, and subsequently extracting the phosphate ions from the column by means of 2 N hydrochloric acid and determining the phosphate by the molybdenum method.

A large amount of work has been carried out by Soviet workers on the application of chromatography to the analysis of alloys. Yu. Yu. Lurye and N. A. Filippova (1948) were the first to demonstrate the possibility of a chromatographic separation of molybdenum from iron by passing a sulfuric acid solution of these elements through a cation exchanger, and selectively extracting the molybdenum with ammonia. I. P. Alimarin and A. M. Medvedeva (1954-1955) have developed a rapid and accurate chromatographic method for separating vanadium and molybdenum from iron; their method consists of extracting these elements from a column of cation exchanger with hydrogen perioxide, which forms complex peracids with molybdenum and vanadium; these same authors showed that it is possible to carry out a selective extraction of molybdenum from a cation exchanger column by means of a solution of citric acid with a pH of 1. T. A. Belyavskaya and E. P. Shkrobot (1955) have developed a number of chromatographic techniques for separating aluminum from iron and titanium, the methods being based on the amphoteric character of aluminum.

A number of papers by Soviet workers has been devoted to the use of ion exchange chromatography for analyzing the alloys of nonferrous metals and for analysis of bronze. I. P. Kharlamov and D. V. Romanov (1952) have shown that it is possible to separate beryllium from aluminum or from copper by means of a solution of ammonium carbonate on the cation exchange resin SBS in the ammonium form. D. I. Ryabchikov and V. E. Bukhtiarov (1951-1952), in connection with the problem of analyzing copper-iron ceramic alloys and bronze, developed a chromatographic technique for separating copper from aluminum and iron, and iron from manganese: iron was selectively eluted with a solution of sodium pyrophosphate in ammoniacal media, while aluminum was selectively eluted with ammonium tartrate in the presence of excess ammonia; aluminum and iron together were eluted with ammonium sulfosalicylate, also in the presence of excess ammonia. We should like to mention the work of Yu. I. Usatenko and O. V. Datsenko (1956) on the chromatographic separation of mixtures of zirconium and iron with hydrochloric acid, and that of I. P. Alimarin, T. A. Belyavskaya, and L. A. Bazhanova (1956) on the separation of titanium from iron and chromium (titanium was selectively eluted with 0.4 N hydrochloric acid, 0.1 sulfuric acid, or a 0.5% solution of Complexone III with a pH of the order of 4; separation is quantitative in the range of ratios of titanium to chromium from 1 : 100 to 10,000 : 1).

A large amount of the work of Soviet workers has been connected with the study of the composition of natural and synthetic salts. M. L. Chepelevetsky, R. E. Osherovich, and S. M. Pevzner (1952) have developed an interesting cation exchange method for determining assimilated phosphoric acid in superphosphates. The suspension of superphosphate is placed with sulfo-coal in the hydrogen form, this simulates cation exchange in the soil and the separation of hydrogen ions by root systems. The extract obtained is passed through a layer of cation exchanger in the hydrogen form; the filtrate obtained is titrated in the presence of bromocresol green and mixed indicator (methyl red and phenolphthalein) and the amount of phosphoric acid calculated by difference. Considerable work has been devoted to chromatographic separation of mixtures of the alkali metals in connection with analysis of glass and silicates. N. K. Shchipakina, E. M. Nemirovskaya, and the author of the present article (1957) showed that a very effective separation of mixtures of the alkali metals occurs on the phosphoric acid cation exchanger RF, and a method has been developed for the direct individual chromatographic separation of sodium and potassium from glasses by solutions of hydrochloric acid of different concentrations. The mean experimental error of the method is 3%; this method cuts down on the time taken to carry out an analysis and simplifies the determination considerably. G. M. Kolosova, N. K. Shchipakina, A. B. Pashkov, and M. M. Senyavin (1956-1957) demonstrated the expediency of using the cation exchanger KU-2 with a high content of divinyl benzene for chromatographic separation of mixtures of sodium and potassium, mixtures of the alkaline earths, and, particularly, mixtures of cesium and sodium. G. B. Maslova, E. A. Suslova, and K. V. Chmutov (1957) have suggested an original method for the chromatographic separation of mixtures of lithium and magnesium, which consists in washing a column of KU-2 containing the test mixture with 0.5 N sodium hydroxide. A. P. Smirnov-Averin, G. B. Kostarev, and I. N. Krot (1957) have recommended a chromatographic method of separating mixtures of rubidium and cesium by eluting a column of the cation exchanger SBS in the sodium form with a 0.5-1% solution of Complexone III with a pH of 5.

A. B. Davankov and V. M. Laufer (1956) have suggested an effective method for concentrating gold and silver from their dilute solutions on the anion exchangers N-O or MN. This work is a further development of the studies of Yu. M. Kostrikina on ion exchange concentration of cations (1950) and of A. A. Kot (1950) on the concentration of anions. N. K. Pshenitsky, K. A. Gladyshevskaya, and L. M. Ryachova (1957) have developed a chromatographic method of separating impurities from metals of the platinum group on the cation exchanger KU-1; the authors succeeded in separating nickel, iron, and lead quantitatively from platinum, rhodium, and iridium, and also in separating copper from iridium and rhodium.

G. D. Eliseeva (1955) using chromatography on paper separated a mixture of the alkali and noble metals, and also a mixture of zinc, beryllium, aluminum, and zirconium; she also used partition chromatography on paper, in particular, for the quantitative determination of manganese, copper, and aluminum in samples of industrial dusts.

Special problems have arisen to confront Soviet workers in connection with the study of nuclear reactions and the peaceful uses of atomic energy. Above all, this was determined by the necessity of developing accurate and rapid methods of determining the amount of uranium in ores and alloys, and of impurities in pure uranium (D. I. Ryabchikov and M. M. Senyavin, 1955). V. K. Markov has developed a technique for determining uranium which is based on partition chromatography, and in conjunction with co-workers, developed a rapid and simple method for determining the content of uranium in natural waters, this method being based on selective sorption of uranium by the anion exchange resin MMG. Chromatographic separation of uranium from impurities has been described in a number of papers, its separation being based on the capacity of uranium to form stable complexes, for example with ammonium carbonate and sodium fluoride, or on the complexing of the impurities by hydrogen peroxide or ethylenediaminetetracetic acid.

Finally, a considerable amount of work by Soviet workers has been devoted to the use of ion exchange chromatography for the analysis of nuclear reaction or fission products. F. I. Pavlotskaya and A. K. Lavrukhina (1956) have studied the effect of the nature of the complexing agent, the pH of the solution, and the concentrations of the elements on the chromatographic separation of the fission products of uranium, thorium, and bismuth produced by protons with an energy of 680 Mev. B. K. Preobrazhensky, O. M. Lilova, A. N. Dobronravova, and E. D. Teterin (1956) have suggested a technique for the chromatographic separation of indicator amounts of the rare elements, in which use is made of ammonium lactate solutions; B. K. Preobrazhensky, A. V. Kalyamin, and O. M. Lilova (1957) established that on the Russian industrial cation exchanger KU-2, exchange takes place very rapidly, approximately 5 times more rapidly than on the cation exchanger Dowex-50. This means that it is not only possible to carry out experiments at room temperature in a number of cases, but to increase the passage of the solution through the column. In particular, the authors were able to separate mixtures of ytterbium and lutecium in 5 minutes on KU-2. A. A. Pozdnyakov (1956) has developed a chromatographic separation of mixtures of isotopes of elements on the yttrium subgroup obtained by fission of ytterbium and hafnium with 660 Mev protons. After removal of the bulk of the irradiated ytterbium by electrolysis on a mercury cathode, and of hafnium by a chromatographic method (absorption of rare earths by a cation exchange from an oxalic acid solution), the test mixture of radioactive rare earths was separated by means of lactic acid.

Let us dwell briefly on new possibilities which have arisen in chromatographic studies as the result of development of work on the peaceful uses of atomic energy. In solving numerous and varied scientific and technological problems, the use of radioactive isotopes has proved to be of limited use for following the path of a chromatographic experiment, for registering it, and for regulating it according to the activity of the filtrates (D.I.Ryabchikov and M. M. Senyavin, 1955). V. B. Gaidadymov and the author of this article (1957) considered the possibility of following the path of a chromatographic experiment by observing reflection of β-radiation from the chromatographic filtrates, and showed that such an approach is feasible by taking as an example the detection of yttrium zones during separation of rare earths by Spedding's method.

When using chromatography for analysis it is essential to separate the mixtures quantitatively. It is simpler to obtain in a pure form a part of the original amount of the test element. Accordingly, combining chromatography with isotope dilution is of interest. V. A. Khalizova and the author of the present article (1957) have shown that when such a method is used for determination of yttrium during chromatographic separation of mixtures of rare earths on a cation exchanger in the copper form, results can be obtained which are in good agreement with the results of x-ray analysis.

As this brief and by no means exhaustive review shows, the chromatographic method is widely used in Russia in all fields of analytical chemistry on a scale ranging from ultramicro analysis (M. N. Pettrikova, 1955) to large setups. Of obvious value is the achievement of Soviet workers in the study and synthesis of sorbents, and in the development of chromatographic theory – on which basis it is possible to forecast the optimum conditions for carrying out chromatographic experiments.

THE ANALYTICAL CHEMISTRY OF THE ACTINOIDS

P. N. Palei

The development of the atomic industry has placed before analytical chemists a large number of completely new problems, and has led to the appearance during recent years of hundreds of papers devoted to the determination of small amounts of uranium, thorium, and transuranium elements in the most varied materials, and to the determination of impurities in pure preparations, etc.

The discovery of specific reactions and analytical methods for the elements of the actinoid family is complicated by the similarity of their chemical properties, which is determined by the structure of the electronic levels (filling of the 5 *f* level) and by their similarity to the lanthanoid family. Actinoids are readily distinguished from the rare earths by the fact that they (particularly the first members of the family) are readily oxidized; differences in oxidation potentials can also be used as a basis for separating them, since in equal valency states they can only be distinguished with difficulty – e.g., Th^{4+}, U^{4+}, and Pu^{4+} can be precipitated, and extracted, form complex compounds, and give color reactions with the same reagents.

A summary of work on the analytical chemistry of thorium and uranium was published by Rodden in 1950 and 1953. The amount of published analytical papers on other actinoids is very small.

This article contains a brief review of the properties and reactions on which chemical methods for separating and determining actinoid elements are based, mainly, those which have been developed or used in the USSR.

URANIUM

Methods of Separation

The absence of completely specific reactions for determining uranium, and the complexity of the composition of most test materials, means that the accuracy of any analysis is determined primarily by the completeness of separation of uranium from interfering elements.

For the separation of uranium, of great importance is complex formation with carbonates, which converts the uranyl cation into a stable complex anion, and distinguishes uranium qualitatively from most metals. The use of this reaction in conjunction with various methods of determination is the subject of many papers at the moment.

It should be pointed out that the uranyl carbonate complex is more stable than many uranyl organic complexes, so that it is possible to separate uranium from iron, copper, etc., by re-extraction of the carbonates into solution from organic solvents containing mixtures of the 8-hydroxy quinoline, diethyldithiocarbamate, and other complexes of uranium and accompanying elements.

On the other hand the low stability of the complex formed between the uranyl ion and a complexing agent such as Complexone III, which is almost universally used, allows one to mask most interfering elements, and separate uranium by reactions which have been earlier-regarded as group reactions and which are not specific for uranium, for example, with diethyldithiocarbamate (N. I. Udaltsova, 1955), with α-nitroso-β-naphthol (I. P. Alimarin, Yu. A. Zolotov, 1957) and also with ammonia (A. A. Pozdnikov, 1954).

The nitrate complexes of uranyl, and their unstable compounds with esters, ketones, tributylphosphate and other organic solvents serve as the basis for numerous extraction methods for separating uranium.

a) Separation by precipitation. Precipitation of U^{4+} ions in an alkaline medium is hardly used at all because of the colloidal nature of the precipitates $U(OH)_4$, added to which these precipitates are slightly soluble in excess alkali (K. Kh. Geier, Kh. Leider, 1957).

Precipitation of the uranyl ion with ammonia, usually with a carrier – ferric hydroxide – is only used for separating uranium from very dilute solutions containing the alkali and alkaline earth elements, copper, zinc, molybdenum, etc. Complete coprecipitation of micro amounts of uranium with $Fe(OH)_3$ is attained at pH 7.5-7.6 (I. E. Starik, F. E. Starik, and A. N. Apollonova, 1957) in the absence of carbonates.

Uranium can be separated from vanadium by precipitation as uranyl phosphate.

Readily filtered, crystalline precipitates, are obtained by precipitation with sulfides in the presence of urotropine (E. A. Ostroumov, 1936, 1939) in the form of "uranium red" – ammonium uranium dihydroxysulfotetrauranate—in this case, only the alkali and alkaline earth elements are removed.

The use of complexones has considerably extended the possibilities of carrying out separations in neutral media: by precipitation with ammonia in the presence of Complexone III, it is possible to separate uranium from iron, vanadium, chromium, molybdenum, tungsten, etc., (A. A. Pozdnyakov, 1954); precipitation with 8-hydroxyquinoline leads to a ready separation from molybdenum (R. Przhibil, 1954), and also from Th, TR, Zr, Al, Ni, Co (Sen-Sarma, Malik, 1954).

The possibilites of separation by precipitation of quadrivalent uranium are considerably greater in acid media.

Phosphates precipitate U^{IV} from weakly-acid solutions – hydrochloric or perchloric; even amounts of uranium of the order of 1 γ can be coprecipitated with the phosphate of Th or Zr, and separated from Fe, Mn, V and many other elements (P. A. Volkov, 1947). U^{VI} is reduced to U^{IV} in this case by means of sodium hydrosulfite, rongalite, divalent chromium, or electrolytically on a mercury cathode.

Uranium can be precipitated by hydrofluoric acid as uranium tetrafluoride, in order to separate it from Zr and Ta, (I. E. Starik, 1956) (from solutions containing the smallest amounts of strong acids, after reduction with zinc).

The double fluorides of uranium (e.g., $NaUF_5$) are very sparingly soluble, even in the presence of strong acids, e.g., 1 N H_2SO_4. Under these conditions Mo, Ti, Ni, Co, Mn, Cu, Fe^{II}, V^{III} are not precipitated; the precipitate washed with a solution of NaF + HF can be titrated with vanadate in sulfuric acid 1 : 2. Reduction of U^{VI} in the presence of fluorides is carried out by means of divalent iron, since, in 3 M HF the real potential of the system Fe^{3+}/Fe^{2+} is 0.22 volt more negative than the system UO_2^{2+}/U^{4+} (V. M. Zvenigorodsky, L. P. Rudina, Ryanicheva, 1955). Reduction can also be affected by means of rongalite (mole for mole of uranium) in the cold, with subsequent precipitation either as the double fluorides, or as the oxalates; in this way it can be separated from many elements (A. A. Grinberg, L. E. Nikolskaya, G. I. Petrzhak, B. V. Ptitsyn, F. M. Filinov, 1957).

The sulfate of quadrivalent uranium is practically insoluble in 47% perchloric acid; it can be precipitated in a pure state from complex solutions, after reduction on a mercury cathode, and can be very accurately titrated permanganometrically (A. I. Ponomarev, M. A. Dragomirova, 1954).

Separation of Fe, Ti, V, Ta, Nb, Zr, Sn, Sb etc., from U^{IV} by means of cupferron, and precipitation of U^{IV}, after reduction, also with cupferron, occurs in 10% and 5% H_2SO_4 respectively. The method in its latest variant (S. V. Elinson, V. A. Oleznyuk, 1955), gives high accuracy.

b) Separation by extraction. Extraction techniques for separating uranium are the most developed methods and the most rapid.

Extraction of uranyl nitrate is essentially improved by using salting out agents: the best of these (from an analytical point of view) are ferric nitrate and particularly ammonium nitrate, which eliminate the harmful influence of sulfates, phosphates, vanadates, molybdates, fluorides (E. I. Dobkina, 1953).

Ether, ethyl acetate, methyl ethyl ketone, tributyl phosphate etc., are used as extractants.

Other compounds of uranium have considerably higher coefficients than the nitrate. Thus, in the presence of NH_4SCH (3%) and NH_4NO_3 (60%) the partition coefficient of uranium between water and methyl ethyl ketone amounts to 2,000 (V. I. Kuznetsov, 1955).

In the presence of α-nitroso-β-naphthol even one treatment with ethyl acetate gives a complete extraction of uranium for a ratio of the volumes of the organic phase to the aqueous phase of 1 : 4. Addition of Complexone III to the aqueous phase, at a pH of about 7.5, leads to a complete separation of uranium from V, Fe, Al, Th, and Zn (I. P. Alimarin, Yu. A. Zolotov, 1957).

Extraction into $CHCl_3$, of the complex of uranium with diethyldithiocarbamate, in the presence of Complexone III, leads to removal of uranium from all elements apart from Cu, Ag, Bi, Hg, Tl, and Se; subsequent re-extraction of uranium into a solution of ammonium carbonate leaves all these elements in the chloroform (N. I. Udaltsova, 1955). A similar method (with preliminary removal of a number of elements with cupferron) was developed later by J. K. Forman, S. J. Riley, and T. D. Smith, 1957.

At a pH of 3.7-7.0 uranium is extracted with a 0.1 M solution of 8-hydroxyquinoline in chloroform; by re-extraction into a solution of ammonium carbonate, complete separation of uranium from Cu, Fe, etc., can be affected (P. N. Palei, N. A. Mirkina, 1954). The use of the halide derivatives of 8-hydroxyquinoline for this purpose was studied by D. Dirsen (1956).

In a number of cases it is more convenient to extract the interferring impurities rather than uranium. Thus, Fe^{III}, V^{V}, W, Cr^{III}, and Sn are completely extracted by means of a mixture of amyl acetate and toluene (1 : 1) from solutions which are 17 N with respect to H_2SO_4 and 1.4 N to HCl; uranium remains in solution, i.e., its partition coefficient is 8,000 times less than that of vanadium for example (V. I. Kuznetsov, 1955).

Separation of uranium from plutonium and fission products by extraction in tributyl phosphate and other solvents, has been studied by Fletcher (1955).

Separation is more effective by carrying out extraction and "washing" (V. M. Mikhailov, 1955), this means that the organic solvent is passed through a separate solution of salting out agent after the test solution. In theory, complete separation of uranium from accompanying elements can be achieved by repeated washings of this kind.

In practice this is achieved by "partition chromatography" on silica gel (V. K. Markov, 1955); a test nitric acid solution is saturated with NH_4NO_3, and is then soaked up on dry, large pore size silica gel, the latter is placed in a column containing silica gel soaked with a solution of NH_4NO_3 in 0.5 N HNO_3; the column is then eluted with ether which has been brought into equilibrium beforehand with the washed solution.

In some work, paper, or paper plus alumina, is used instead of silica gel (e.g., A. F. Williams, 1952). Differences in sorption also play an important part in this case.

c) Separation by sorption. When paper is soaked with test solution, separation of ions occurs because of differences in the sorption properties of the ions; this phenomenon can be enhanced by the appropriate choice of solvent and composition of the test solutions, with subsequent washing with reagents, etc. The use of organic solvents for washing makes this technique similar to partition chromatography on cellulose. A large amount of work has been devoted to variants of this technique (e.g., that of G. D. Eliseeva, 1955), the work being mainly of a qualitative nature.

Considerably more complete separation is possible by using sorption on special synthetic resins, e.g., KU-2, i.e., by using ion-exchange chromatography.

As long ago as 1949, B. Hilger described an ion-exchange separation of uranium from sulfate and phosphage ions which interfere with extraction of uranyl nitrate. Amphoteric metals and metals which form complex anions are readily removed.

Passage of a weak acid solution containing uranium and impurities through a cation exchange in the H-form removes all anions; by subsequent washing of the column with alkali, such amphoteric elements as Al, V, and Mo can be removed, while by washing with ammonia, copper can also be removed; uranium remains on the resin as the diuranate and is readily eluted by a more concentrated solution of acid.

For analysis of carbon ash containing U, V, and Mo, a method was developed (N. T. Voskresenskaya, 1955) which was based on sorption of U, V, and Mo on the cation exchanger PFSK from 0.15 N acid, and washing with water and 5% H_2O_2, which elutes V and Mo as the peracids. Uranium was then eluted with 5% H_2SO_4.

Uranium was determined in alloys and polymetallic ores by using the cation exchanger KU-2 in the sodium form (Z. K. Mikhailova, 1955), this resin held back all the uranium from solutions with a pH of 1.8-2.0 containing excess of Complexone III, while Fe, V, Mo, W, Cu, and Pb passed into the filtrate.

Many complexes of uranium can be used for its selective extraction from cation exchange resins. Ammonium carbonate has been used – after washing off V and Al with 10% ammonia (D. I. Ryabchikov, M. M. Senyavin, Z. K. Mikhailova, V. K. Sarygina, 1952); ammonium acetate has been used at a pH of 5.0-5.5 (N. M. Sobinyakova, E. A. Rubinshtein, L. P. Maksheeva, 1955); or sodium fluoride (V. A. Khalizova, E. P. Smirnova, 1955) for removing uranium from large amounts of iron. In all these cases KU-2 was used.

Uranium can be extracted from solutions containing its anionic complexes by means of anion exchangers; thus, the carbonate complex, usually in natural waters, can be absorbed by the resin MMG-1 in the bicarbonate form (V. K. Markov, 1955); this technique is suitable for very small amounts of uranium of the order of 1 γ; the resin is dissolved in concentrated hydrochloric acid and the solution analyzed by the luminescence method.

Amberlite IRA-400 in the chloride form absorbs all the uranium and part of the vanadium from soda solutions; vanadiun is eluted with excess 10 γ soda solution, while uranium is removed by means of NaCl (T. K. S. Marsi, 1957).

d) Separation by volatilization. H. J. Emeleus, et al., as long ago as 1948 showed that by treating an uranium compound with bromine trifluoride, the uranium is transformed into the volatile hexafluoride, while uranium fission products are converted into nonvolatile compounds. This technique has been used for analysis of uranium minerals and can be used for determination of a number of small impurities in uranium. Although all the operation can be readily carried out in a simple quartz apparatus – in the absence of moisture – the method has not yet been widely used.

e) Separation of uranium by electrolysis – See p. 675.

METHODS FOR DETERMINATION OF URANIUM

a) Gravimetric methods. The usual compound of uranium used for its gravimetric determination is U_3O_8 – uranoso uranic oxide, which is obtained by calcining, with plenty of access to air, practically all the precipitates used for separating uranium in a pure form: ammonium diuranate, the 8-hydroxyquinolate, the peroxide (uranyl peruranate), the oxalate, the cupferronate, etc. The temperature conditions necessary for converting the 15 most important analytical precipitates of uranium into U_3O_8 have been studied by Duval (K. Duval, 1948); he found that above 946°, U_3O_8 starts to change into UO_2; below 750-800° conversion of most precipitates into U_3O_8 proceeds slowly.

The precipitate of uranium 8-hydroxyquinolate $UO_2(C_9H_6ON)_2 \cdot C_9H_7ON$, which is deposited from 5% acetic solution, and dried at 105-130° (F. Hecht, V. Reich Rorvig, 1929) is a good gravimetric form, but is rarely used.

For materials containing more than 5% uranium the most convenient method of separating uranium is to precipitate it as the cupferronate after reduction by sodium hydrosulfite (C. V. Elinson, V. A. Oleznyuk, 1955 and 1957) and then calcine it to give U_3O_8.

Gravimetric methods are only used for rich and relatively pure uranium materials where maximum accuracy is important. In this respect the peroxide method gives the best results.

b). Volumetric methods. Two groups of methods are of essential importance for the volumetric determination of uranium: the first is the reduction of uranium to U^{IV} followed by titration with oxidizing agents, the second method is precipitation and titration of the anion which forms part of a precipitate.

Precipitation of the uranyl ion as its molybdate, dissolving the latter in hydrochloric acid, and then reducing the molybdenum with zinc amalgam to Mo^{III}, followed by titration with ammonium vanadate, was worked out long ago by V. S. Syrokomsky and Yu. V. Klimenko (1940).

Titration with potassium bromate of the three molecules of 8-hydroxyquinoline forming part of uranyl hydroxyquinolate, has the advantage that 12 equivalents of bromine are required for titration of 1 mole of uranium.

The precipitate of UO_2SeO_3 formed by selenious acid in 50% alcoholic solution at a pH of 4-5, can be titrated iodometrically (M. K. Joshi, 1956).

Oxidimetric titration of U^{IV} is the most widely used method both for large and small amounts of uranium. Potassium permanganate and dichromate, cerium sulfate (IV) and ammonium vanadate have been used as oxidizing agents.

V. S. Syrokomsky (1950) has shown that in sulfuric acid solutions the potential of the system V^V/V^{IV} increases rapidly with acid concentration, and, in 27 N H_2SO_4, reaches a value of +1.45 volt; on this basis a new volumetric technique – vanadometry – has been developed.

The use of phenylanthranilic acid as an indicator has made it possible to titrate (with ammonium vanadate) very clearly small amounts of U^{IV} of the order 0.1 mg, in sulfuric acid 1 : 2 with an accuracy of ± 1% (I. P. Alimarin, 1952).

Usually, zinc, cadmium, silver, lead, or the mercury cathode are used for reducing U^{VI} to U^{IV}. For vanadometric determination it is advantageous to reduce the uranium by means of a bismuth reducer, since on increasing the concentration of sulfuric acid, the potential of metallic bismuth drops, while the potential of the system $U^{VI}U^{IV}$ increases (P. N. Palei, N. I. Gusev, 1954).

All metallic reducing agents, as well at Ti^{III} and Cr^{II} reduce uranium, although only partially, to U^{III}; this is not a source of interference during potentiometric titration, for titration with indicators it is necessary to oxidize U^{III} to U^{IV} beforehand by air. It is considered that U^{IV} is hardly oxidized at all by air, but this is only true for very pure solutions of U^{IV} in the dark. In the light, depending on the intensity of its ultraviolet component, aerial oxidization increases; in the presence of catalysts (Mo, Cu), even in amounts which are only 0.01% of the uranium, loss of U^{IV} may be of the order of a few dozen percent (E. V. Palei-Rengarten, 1953).

A convenient method for the oxidimetric determination of uranium is its precipitation as $U(HPO_4)_2 \cdot H_2O$ by reduction with sodium hydrosulfite in a weakly acid solution containing excess phosphates (P.A. Volkov, 1947). After filtering off the precipitate, it is dissolved in sulfuric acid and the quadrivalent uranium determined vanadometrically.

For establishing the equivalence point during oxidimetric methods of determing U^{IV}, it is expedient to use indicator electrodes of the usual type which measure E_h, or the "the dead point method"*; of interest is a new method suggested by Walisch – "Polarvoltriya" (1957), i.e., titration up to the point where there is a jump in the differences in potential between polarized platinum electrodes.

Oxidation of U^{IV} by electrolytically generated oxidizing agents (e.g., Br from $FeBr_3$ – V. N. Kerson, 1953) has made it possible to increase the limit of accurate determination of uranium to a few micrograms.

All oxidimetric methods necessitate preliminary separation of uranium from other readily oxidizable elements, while in the case of electrochemical indicators, a number of other elements which exhibit variable valence must also be absent. In this connection, therefore, of interest is the possibility of carrying out amperometric titration (Yu. V. Morachevsky, I. A. Tserkovnitskaya, 1957) of U^{IV} with vanadate in which complexing agents are used, which remove interfering elements as stable, nonoxidizable compounds; o-phenanthroline for iron, Complexone III for Cr, Ni, Bi, Pb etc. The method is also suitable for microgram amounts of uranium.

c) Polarographic methods. The mechanism of the complete reduction (and oxidation) of uranium $U^{VI} - U^V - U^{IV} - U^{III}$) on a mercury cathode and on solid electrodes cannot yet be regarded as being completely clarified, despite the large amount of work – including work by Soviet workers (Frumkin, Veselovsky) – devoted to this question.

The first stage of the reduction of UO_2^+ is reversible and involves one electron. In strongly acid solutions (1-2 M) the stage UO_2^+ UO_2^{2+} disappears, since under these conditions UO_2^{2+} disproportionates instantaneously; the first wave becomes a two electron stage, which is convenient from the point of view of increasing sensitivity.

Many elements interfere with polarographic determination of uranium, and chemical separation of these elements takes considerable time. Direct determination of uranium in a test solution is possible by choosing a supporting electrolyte which contains complexing agents either for the interfering elements or for uranium itself. Thus, in the presence of Fe, Ti, V, Cu, Mo etc., determination is possible (S. I. Sinyakova, 1955) when Fe^{3+} is reduced by hydrazine sulfate, which simultaneously precipitates copper: interference by molybdenum can be suppressed by using lactic acid, while interference by titanium can be suppressed by chromotropic acid; by adding excess vanadium, use can be made of its effect on the height of the uranium wave for increasing the sensitivity of the method. In a 0.01 M solution of quadrivalent vanadium it is possible to determine 0.01 to 1.0 mg of uranium quantitatively (Yu. V. Morachevsky, A. A. Sakharov, 1957).

In the form of its carbonate complex, uranium can be quantitatively determined in the presence of Complexone III which complexes all interfering elements apart from Pb and Cu (R. Przhibil, 1954).

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*Direct translation – Publisher.

Of interest is the possibility of determining uranium polarographically in nonaqueous solutions obtained during treatment of irradiated uranium; a solution of tributylphosphate in kerosine is diluted with glacial acetic acid and polarograms taken in a supporting electrolyte of lithium perchlorate (D. J. Fisher, P. F. Thomason, 1956).

The use of an oscillograph in polarography has meant that it is possible to increase the rate of change of voltage applied to the polarographic cell a hundred times, and also that it is possible to increase the sensitivity of the method one and one half times; for uranium this means that it is possible to determine concentrations of 10^{-6}% of uranium with an accuracy of ± 5%, and also use polarography for following changes in uranium concentration with time. In contrast to normal polarography there is no need in this case to remove oxygen from test solutions (Ya. P. Gokhshtein, 1955).

d) Photometric methods. The most sensitive reagents for uranium are dialkldithiocarbamates, dibenzoylmethane, arsenazo, and thoron.

Sodium diethyldithiocarbamate which is used for separating uranium from many elements, gives a compound with the uranyl ion (V. M. Kazakov, 1953) which has a molar extinction coefficient $\alpha_{380} = 4050$ in chloroform; it allows 1 γ of U in 10 ml to be determined.

Dibenzoylmethane in an aqueous pyridine medium, in the presence of Complexone III and tartaric acid, gives a very sensitive color (415 mμ); a method (P. Blanke, 1957) has been developed for the determination of 0.05 to 20% of uranium in very complex ores, containing columbite, tantalite, and other minerals.

V. I. Kuznetsov as long ago as 1941 developed a reagent specially synthesized for uranium — arsenazo: benzene-2-arsonic acid < 1-azo-2 > 1,8-dihydroxynaphthalene-3,6-disulfonic acid. The reagent gives a blue color with uranyl ions in the presence of urotropine (pH 4.5-5.5); the limit of identification is 0.2 γ U, while the limiting dilution is $1 : 5 \times 10^6$ (V. I. Kuznetsov, 1952, 1957). UU^{IV} with the same reagent, at an acidity of 0.02-0.05 N, gives a violet color; the limit of identification is 1-2 γ. Both colors change to rose under the influence of H_2O_2. Cu, Th, V, Al, TR, etc., also give colored compounds with arsenazo.

Another reagent – thoron – also developed by V. I. Kuznetsov possesses the highest sensitivity; thoron is benzene-2-arsonic acid < 1-azo-2 > hydroxynaphthalene-3, 6-disulfonic acid. The reagent gives a rose color with U^{IV} in hydrochloric acid media. U^{VI} is reduced to U^{IV} by means of iodides, and the iodine liberated by blowing nitrogen through the solution, up to 10^{-8} g of U in 1 ml can be determined. Al, Fe^{III}, Zn, Ce^{III}, La, Be, Ca do not affect the determination, U^{VI} does not interfere at ratios of U^{VI} to U^{IV} of 1000 : 1, V^{III} does not interfere at ratios of V^{III} to U^{IV} of 16 : 1, while Cr^{III} does not interfere at ratios of Cr^{III} to U^{IV} of up to 6 : 1, and Th at ratios up to 200 : 1; SO_4^{2-}, NO_3^-, F^-, phosphates, oxalates, and organic materials should be completely removed (A. V. Nikolaev, A. A. Sorokina, 1955).

On the basis of this reagent, Formen, et al., (1957) has developed a method for determining microgram amounts of uranium in complex materials by carrying out colorimetric determination in 80% acetone which doubles the molar extinction coefficient. The method includes complicated purification from other elements.

e) Spectrographic methods. The low sensitivity of the spectrographic method for uranium, coupled with the great diversity of the composition of test materials, which affect the intensity of the spectral lines of uranium, complicate the problem of determining small amounts of uranium.

V. K. Prokofvev and co-workers (1955) used preliminary separation of uranium on a cation exchanger whereby it was possible to determine down to 10^{-4}% uranium.

Direct determination in an arc, using the line 4341.69 A enabled N. P. Ivanov (1954) to determine down to 0.001% of uranium in ores on the ISP-51 apparatus, the reproducibility was ± 4-5%, but this was only possible under conditions where the spectra were compared with those of standards of roughly the same composition.

N. G. Morozova (1957) using briquetting with copper powder and using M_0 as an internal standard, obtained a sensitivity of 0.005% and a reproducbility of ±5%.

The use of the light isotopes of uranium as internal standards (N. P. Ivanov, 1955) has appreciably increased the universality of the spectrographic determination of uranium in various products. The similarity between the chemical and physical properties of both isotopes determines the similarity in their behavior during evaporation and excitation processes; the relative intensity of the two "isotopic components" of the analytical line, depends to only a very small extent on changes in evaporation or excitation conditions of the uranium atoms in the source, and is determined only by the relative concentrations of the isotopes in the sample.

Systematic studies of the spectra of U^{233} and U^{235} on an ISP-51 spectograph (with a UF-85 camera) showed that the line 4244 A with an isotope shift of 0.23 A, is the most suitable line for analytical purposes. It was shown that the relative intensity of the lines of the isotopes is independent of the electrode dimensions, the weight of sample taken, changes in current, strength, etc. Evaporation curves in an A. C. for U^{238} and U^{235} from tests of different composition proved to be identical. All this means that there is no need to use the usual method of three standards, and also, that it is possible, with considerable increase in speed of analysis, to achieve an accuracy of 3-4%, i.e., to get agreement with a chemical method for determinations of 1.0-0.005% uranium. The amount of the light isotopes used is negligible – only about 1 mg of a light isotope is necessary for 250 determinations. The method is being used for production control.

f) Luminescence analysis. The capacity of certain uranium compounds to convert ultraviolet radiation into visible light means that it is possible to detect and determine extremely small amounts of uranium down to 10^{-9} g. The luminescence method has found wide application in sanitary analysis and in geochemical research. Various techniques for separating small amounts of uranium and for purifying them from interfering elements are described in the review by Rodden.

For separating uranium (10^{-4}-10^{-5}%) from rocks, L.V. Tauson (1956) used the hydrosulfite-phosphate method of P. Volkov (see above), using zirconium as a carrier for uranium.

For separating uranium from sea water it has been suggested that it can be coprecipitated from an acidified solution with a precipitate of methyl violet thiocyanate (V. I. Kuznetsov, T. G. Akimova, 1957), which quantitatively traps uranium at concentrations of the latter of 1 γ per liter.

Of all the compounds of uranium the one that gives the highest sensitivity, i.e., the brightest illumination under the ultraviolet, is a solution (melt) of it in sodium fluoride.

The nature of the centers of illumination of the beads of sodium fluoride activated by uranium has been established by T. S. Dobrolyubskaya (1956).

The effect of various elements on the intensity of the illumination of uranium in sodium fluoride has been studied by I. E. Starik, F. E. Starik, L. Ya. Artashenok, G. B. Kostyrev, V. N. Kosyakov, and A. Ya. Krylov (1956).

The accuracy of measurements of the luminesence of beads with uranium, when the FM-42 photometer made by the State Optical Institute is used, amounts to 1% relative error.

The luminesence of salts of uranium in aqueous solutions is very much weaker and is hardly used at all. Only recently Tomich (1955) demonstrated the possibility of measuring, with an accuracy of ± 5%, amounts of uranium from 0.5-10 γ in a compound with morine in the presence of acetone.

Determination of Impurities in Pure Uranium Preparations

Methods with a sensitivity of 10^{-5}% have been used for the determination of neutron-active impurities (Li, B, Be, Cd, etc.) in pure uranium. Chemical methods of removing impurities, e.g., distillation of boron as methylborate, are extremely difficult, and furthermore, necessitate reagents of exceptional purity. Normal spectrographic methods are not sufficiently sensitive; it was necessary to increase this sensitivity.

The problem was solved (S.L. Mandelshtam, N. N. Semenov, Z. M. Turovtseva, 1956; A. N. Zaidel, N. I. Kalitcevsky, L. V. Lipis, M. P. Chaika, and Yu. I. Belyaev, 1956) by the so-called "evaporation method," i.e., by splitting up the processes occurring at the light source into three stages: evaporation of impurities from the test mixture, their condensation on a cold capsule, and excitation of the spectra of the distilled impurities.

Such a separation technique made it possible, in the first instance, to increase the weight of sample taken to 200 mg and more; secondly, to exclude from the spectrogram all the multilinear spectrum of uranium; thirdly, to lower the requirements for the purity of electrode materials considerably.

As a result, the sensitivity of the spectrographic determination of impurities was increased to 5×10^{-6}% for boron, to 1×10^{-5}% for manganese, to 5×10^{-5}% for cobalt, and to 2×10^{-6}% for lithium, i.e., to orders several times higher than that of Scribner's method. For some materials and impurities it is convenient to carry out the distillation under vacuum, or to introduce into the test small amounts of a carrier (gallium, gold) and internal standards. The evaporation method has a mean arithmetic error of about 10%. One of the basic conditions for the successful application of the method is the correct choice of evaporation temperature of the impurites, which should not be too near to the temperature at which the base material itself — uranium oxide starts to distill.

The evaporation method which possesses many advantages over the usual spectrographic methods, is applicable to other objects (N. I. Kaliteevsky, A. A. Lipovsky, A. N. Razumovsky, P. N. Yakimova, 1957).

Nevertheless, in the case of impurities which give oxides which are only slightly volatile e.g., ThO_2, the method is not applicable. In such cases one has to resort to chemical separation. Thorium for example, can be separated from large amounts of uranium by precipitation with cinnamic, anisic, metacresoxyacetic acids (Ragava Rao, et al., 1951, 1952).

For rare earths which have particularly high values for neutron capture cross section (gadolinium, europium) the sensitivity of the evaporation method is not high enough. These elements are separated chemically from large samples of uranium by making use of the low solubility of the fluorides of these elements, the uranium being kept in solution by means of bicarbonates, etc., (D. I. Ryabchikov, F. I. Pavlotskaya, 1948). Cerium is normally used as carrier. Individual determination of all the elements of the rare earth group in the precipitate which separates out is usually unnecessary: it is sufficient to determine one of the most widely distributed elements (usually neodymium), so that from their known ratios in a natural mixture it is possible to calculate gadolinium and the other rare earths in the uranium.

Determination of neodymium in the cerium precipitate is carried out by x-ray spectrography (E. E. Vainshtein, 1948); this method gives an accuracy of 4-6% for a neodymium content in the mixture of 0.1% and higher. In contrast to the optical spectrum, the results of x-ray spectrography are consistent for any test composition.

THORIUM

Thorium exhibits a valence of four. This limits the number of possible analytical methods — oxidimetry, polarography, etc., are excluded. Until recently methods for isolating and determining thorium were almost exclusively based on precipitation reactions. In recent years chromatographic, extraction, and complexometric methods have appeared; while a number of new precipitants have essentially simplified the old and very complicated techniques.

Methods of Separation

a) Separation by precipitation. Precipitation of thorium hydroxide by alkalis is of very limited application, since the elements which usually accompany thorium are also precipitated, such elements include the rare earths, zirconium, uranium, etc. Nevertheless, if buffer mixtures of pyridine and its nitrate are used for precipitating the thorium, completely satisfactory removal of thorium from the rare earths is possible (E. A. Ostroumov, 1946, 1957).

Precipitation of thorium with excess oxalic acid from 1-2 N HCl, HNO_3, or $HClO_4$, as $Th(C_2O_4)_2 \cdot 6H_2O$, enables thorium to be separated from most elements with the exception of the rare earths. U^{VI}, Zr, Ta, and Nb are readily removed. Sulfates and phosphates interfere.

Pure and readily filtrable precipitates of thorium oxalate are obtained by slow hydrolysis with acetone dioxalic acid (F. V. Zaikovsky, L. I. Gerhardt, 1957). The solubility of $Th(C_2O_4)_2 \cdot 6H_2O$ is half of that of the corresponding uranium salt (A. A. Grinberg, G. I. Petrzhak, 1956).

By precipitating thorium from moderately acid solutions with excess hydrofluoric acid as $ThF_4 \cdot 8H_2O$, thorium can be separated from elements which form soluble fluoride complexes — Zr, Hf, Nb, Ta, and W. In the presence of large amounts of potassium, potassium fluorozirconate and potassium fluorotitanate are precipitated.

Separation of zirconium from thorium by precipitation as oxalates and fluorides has been compared by V. I. Kuznetsov and I. V. Nikolskaya (1957); trapping of zirconium by the precipitate amounts to 1.6-1.8% of the amount of zirconium taken, i.e., the methods are of equal efficiency from the point of the separation achieved.

Separation of thorium from the rare earths, but not from Zr, Ti, Ce^{IV} can be achieved by precipitation with potassium iodate from 0.5-0.6 N nitric acid as the readily filtrable precipitate $4Th(IO_3)_4 \cdot KIO_3 \cdot 18H_2O$ (Yu. A. Chernikhov and T. A. Uspenskaya, 1940; L. E. Kaufman, 1936).

Thorium peroxide, which was examined as long ago as 1900 by Pisarzhevsky, during precipitation from acid solutions, only traps zirconium and titanium; $ThO_2SO_4 \cdot 3H_2O$ is precipitated from 1 N H_2SO_4. Of the rare earths cerium is coprecipitated in small amounts.

From solutions not containing excess mineral acid, metanitrobenzoic acid precipitates thorium as $Th(C_6H_4NO_2COO)_4$. By double precipitation it is possible to separate thorium from the rare earths, zirconium, iron and large amounts of uranium.

R. Rao has studied the precipitation of thorium by many reagents: removal from uranium by means of anisic acid (1951) and by cinnamic acid – which was particularly effective (1951); removal from the rare earths by means of sodium sulfanilate (1951), sodium naphthionate (1950), and ammonium benzoate (1952).

The stable complex of thorium with Complexone III has been used by Sen Sanna and Malik for keeping thorium in solution during precipitation of uranium with 8-hydroxyquinoline at pH 5.3 (1954).

Precipitation with sodium benzenesulfinate from 0.5 N hydrochloric or nitric acid removes thorium from 100 times its amount of the rare earths, Be, Al; uranium (VI) is not precipitated at a ratio of 1 : 16, titanium is not precipitated at 1 : 10; iron is coprecipitated (II and III) (I. P. Alimarin, S. S. Alekberov, 1957).

Precipitation with phytin from 6 N nitric or hydrochloric acid removes thorium from the rare earths (I. P. Alimarin, L. Z. Kozel, 1957).

Precipitation with phytic acid in the presence of oxalic acid and 6 N nitric acid, removes thorium from Ti, Zr, U, Fe, and the rare earths. On calcining, the precipitate is converted into $Th(PO_3)_4$. This method has been used for determining Th in monazite concentrates (D. I. Ryabchikov, V. K. Belyaeva, A. N. Ermakov, 1957).

b) Separation by extraction. The amount of work published on extraction of thorium for analytical purposes is surprisingly small. Mention can be made of the extraction of thorium nitrate with mesityl oxide; only U^{VI} and some Zr and V are extracted with the thorium. The use of $Al(NO_3)_3$ as a salting out agent allows one to extract without removing sulfates and phosphates (Kh. Levin, F. S. Grimaldi, 1954).

From carbonate solutions at a pH of about 4 it is possible to effect complete extraction of thorium as its cupferronate, and, at the same time, remove it from uranium (A. S. Ekkert, R. V. Bein, 1945).

Many ketones have been suggested for extracting thorium nitrate and at the same time isolate it from the rare earths, Zr, and Ca; methyl butyl ketone is the best (Templeton, Hall, 1947).

Extraction of thorium nitrate by tributylphosphate has been studied in detail; by varying its concentration in an inert diluter and varying the concentration of HNO_3 in the aqueous phase it is possible to separate thorium from uranium (H. A. S. McKay, 1955) and from fission products (A. T. Gresky, 1955).

Stable inner complex compounds of thorium with diketones, e.g., thiophenecarbonyltrifluoroacetone (TTA), can be extracted by benzene (R. A. Dei R. V. Stauton, 1956); this fact can be used for separating thorium from di-and trivalent ions, e.g., UO_2^{2+} and the rare earths.

c) Chromatographic methods. Separation of thorium from U, Fe, Al, Ca, Mg, and Cu (D. Dirsen, 1950) is based on the relation between the sorbability of ions and the size of their charges. A detailed study has been made of the absorption of thorium ions by a number of sulfonate cation exchangers in the hydrogen, potassium, and magnesium forms, under static and dynamic conditions. From 0.5-1.0 N solutions of HCl or HNO_3, thorium is selectively absorbed and is readily removed from uranium; the method is suitable for extracting the thorium isotope (UX_1) from concentrated uranium solutions. With increasing pH the capacity of thorium to be absorbed by sulfonate cation exchangers disappears sooner than in the case of uranium; at pH 3.8-4.5 selective absorption of uranyl ions is achieved.

A study has also been made of the possibility of effecting a chromatographic separation of the acetates of U^{VI} and Th on the weakly basic anions exchanger Wofatite (B. P. Nikolsky, V. I. Paramonova, A. F. Vyugina, 1955). The anionic uranium acetate complex becomes more stable with increasing concentration of thorium acetate.

Thorium sorbed on a cellulose column can be eluted with ether containing 12.5% (by volume) of nitric acid, after which Zr is removed with excess oxalic acid, while uranium is washed off with 3% nitric acid (N. F. Kimber, 1952).

Methods of Determination

a) Gravimetric methods. Usually the gravimetric form used for determining thorium is the oxide which is obtained by calcining the hydroxide, peroxide, oxalate, and nitrate. Precipitates containing sulfur lose it on calcining slowly and not completely. Calcining with oxalic acid allows one to convert many organic thorium compounds – 8-hydroxyquinolate, cupferronate, meta-nitrobenzoate, salicylate, etc., – quantitatively into the oxide.

Thorium benzenesulfinate can be dried at 110° and weighed as $Th(C_6H_5SO_2)_4$ (I. P. Alimarin, S. S. Alekberov, 1957).

On calcining thorium phytinate at 800-1000° it is converted into the meta-phosphate $Th(PO_3)_4$; the method ensures an accuracy of ±0.1% (see above – D. I. Ryabchikov, et al., 1957).

Thorium 8-hydroxyquinolate precipitated with excess 8-hydroxyquinoline and dried at 130° for two hours, has the formula $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$. The error is usually ±0.2%. On drying over a prolonged period one molecule of 8-hydroxyquinoline is lost (F. Hecht, V. Ermann, 1935).

b) Volumetric methods. The methods cited in Rodden's review are almost exclusively indirect methods, which consist in titrating the anions of certain thorium precipitates: the molybdate (oxidimetrically after reduction of the molybdenum), oxalate (oxidimetrically with oxalic acid, 8-hydroxyquinolate (iodometrically, 8-hydroxyquinoline). More effective, direct methods are known, however.

Thus, use has been made of the formation of the very stable complex of thorium and Complexone III; by high-frequency titration it has been established that the molar ratio of thorium to Complexone III is 1 : 1; the compound $NH_4[Th \cdot TrOH] \cdot H_2O$ is obtained at pH 7 (D. I. Ryabchikov, V. K. Belyaeva, 1957).

The hydrogen ions which are liberated during formation of the complex allows one to use high-frequency conductometry to establish the equivalence point, and an oscillograph as a null instrument permits titration of 0.0001-0.0002 M solutions of thorium with an accuracy of up to 0.5% (R. Hara, P. West, 1955).

Several methods have been suggested for carrying out visual titration with a solution of Complexone III at pH 2.3-3.4, using p-alizarin Red S as indicator, or even better, pyrocatechin violet (I. Chirk, M. Malat, V. Suk, 1955) and 1-(2-pyridylazo)-2-naphthol (A. I. Busev and co-workers, 1957). Ca, Mg, Sr, Ba, La, Cr, Mn, Co, Ag, Zn, Cd, and UO_2^{2+} do not interfere; Ti, Zr, V, Fe, Ni, Cu, Sn, Pb, and Bi interfere.

On the basis of the high light absorption coefficient of the copper complex, an automatic spectrophotometric titration of thorium with a solution of Complexone III in the presence of copper at pH 3.1 has been worked out (Kh. V. Malmshtadt, E. K. Gorbandt, 1954).

Mention should also be made of the following direct titration methods; titration with potassium ferrocyanide in 30% alcohol (F. M. Shemyakin, V. A. Volkova, 1937); high-frequency titration with oxalic acid (V. I. Bledel, Kh. V. Malmshtadt, 1951); and nephelometric titration with potassium phthalate (Bobtelsky, Bar-Gadda, 1953).

c) Photometric methods. The reaction between thorium and quinalizarin suggested as long ago as 1933 (A. S. Komarovsky, I. M. Korenman) possesses a high sensitivity – the limit of identification is 0.18 γ Th. In weakly-acid solution containing 60% acetone, light absorption is measured at 580-600 mμ. Fe, Ti, Zr interfere (A. Purustam, 1955).

The reagent arsenazo gives a violet color with thorium in neutral media (V. I. Kuznetsov, 1947); it is convenient to measure light absorption at 546 mμ. In the presence of Zr, Ti, and the rare earths thorium is determined on a background of tartaric acid (F. V. Zaikovsky, L. I. Gerhardt, 1957).

Thoron is the most suitable reagent for determining micro amounts of thorium (see above). The optimum pH range is 0.3-1.0; the limit of identification is 1 γ, while the limiting dilution is 1 : 10^6. Thorium reacts with thoron in the proportion of 1 : 2, the complex formation constant $K = (7.9 \pm 0.9) \times 10^9$ (L. P. Adamovich, V. M. Rutman, 1954). Fe^{III} interferes and is reduced with hydroxylamine; Zr is removed with oxalic acid, while

U^{IV} is converted beforehand into UO_2^{2+} by oxidation – heating with $HClO_4$. Mn, Mg, Zn, Al, Cu, and Ce and the rare earths do not interfere (A. Mayer, J. Bradshaw, 1952). Light absorption is measured at 545 mμ.

The precipitate thorium forms with para-arsonic acid is intensely colored, and can be dissolved in alkali and its color measured at 460 mμ (F. S. Grimaldi, I. J. Fairchild, 1945). The experimental error is ± 10%.

Thorium 8-hydroxyquinolate is suitable for photometric determinations when in solution in acetone (R. O. Ragava, N. Esvarapaiyana, 1954).

d) Spectrographic methods. Spectrographic determination of small amounts of thorium is just as difficult as that of small amounts of uranium. Nevertheless, after separation on a cellulose column and coprecipitation with lanthanum as the oxalates, it is possible to determine thorium at contents in the ore of 0.2-1 × 10^{-3}% on a test sample of 1 g using the 2837.3 A line, and using the lanthanum line 2821.04 as an internal standard. The error is ± 3% (G. V. J. Kingsberg, B. V. F. Temple, 1952).

Determination of Impurities in Pure Thorium

Since thorium oxide is one of the most nonvolatile oxides it is evident that the "evaporation method" which was developed for the spectrographic determination of impurities in uranium, can also be successfully used for thorium.

The absence of oxidation – reduction reactions for thorium means that it is possible to determine a number of elements in it by the polarographic method, without separation of these elements; thus, zinc can be determined at a content of 1 × 10^{-3}% of zinc, the thorium being kept in alkaline solution by sulfosalicylic acid (J. H. Peterson, G. V. Banks, 1948).

TRANSURANIUM ELEMENTS

In equivalence states the elements of the actinoid group have very similar properties; the main difference between them is the stability of their valence forms.

In Seaborg's table (reproduced in Table 1) the most stable oxidation states under normal conditions are shown in italics.

A quantitative expression of this regularity in 1 M aqueous solutions, for uranium and the transuranium elements, is given in Latimer's table (Table 2).

TABLE 1

Element	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf
Oxidation state	*3*	(3)	(3)	3	3	3	*3*	3	*3*	3
		4	4	4	4	*4*	(4)		4	
			5	5	*5*	5	5			
				6	6	6	6			

TABLE 2

Element	Normal potential	
	III/IV	IV/VI
92 Uranium	+0.63	−0.33
93 Neptunium	−0.14	−0.94
94 Plutonium	−0.98	−1.04
95 Americium	−2.32	−1.34
96 Curium	< −2	–

These differences in the potentials means that it is possible, in the same solution, e.g., at E_h-0.5 volt, to get neptunium in a quadrivalent state, plutonium and americium in a trivalent state, and uranium in a sexivalent state.

Many reactions have been studied whereby analogies can be drawn between the actinoids in the trivalent state and lanthanum, between the quadrivalent state and thorium, and the sexivalent state and U^{VI}. A study of the reactions of quinquevalent neptunium is casting more and more light on the properties of the states of Pu^V and U^V of low stability.

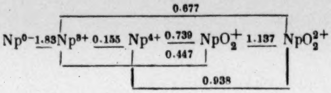
In similar valence states the actinoids differ from each other, with respect to the degree of hydration and the sorption energies of the ions, the stabilities of the complex compounds, the absorption spectra, and, finally, with respect to half-life periods and radiation energies.

Thus, there is a sufficient basis for developing analytical techniques; it is therefore a matter of surprise that the number of papers which have appeared in recent years on the analytical chemistry of the transuranium elements is so small.

NEPTUNIUM

A review of work on the analytical chemistry of neptunium was published recently in Russian (I. P. Alimarin, Yu. A. Zolotov, 1957), consequently we shall only deal with the most important results here.

The oxidation – reduction potentials of neptunium ions in 1 M $HClO_4$ are:



Np^{III} is only slightly more stable than U^{III}; it is readily oxidized by atmospheric oxygen. Solutions of Np^{III} are prepared from the highest oxidation states by electrolytic reduction; in 1 M HCl, Np^{IV} is reduced by rongalite (1%) and $N_2H_4 \cdot 2HCl$(2%), in 30 minutes to the extent of 95%; in 1 M HNO_3 reduction is incomplete (70%) (A. D. Gelman, M. P. Mefodyeva, 1957).

Np^{IV} is slowly oxidized by oxygen in 1 M HCl or $HClO_4$, in HNO_3 oxidation is more rapid. It is stable in 1 M H_2SO_4. It is a strong complexing agent: sulfate, chloride, and nitrate complexes are known, Np^{IV} solutions are obtained by reduction of Np^V or Np^{VI} by means of SO_2, hydroxylamine, hydrazine, iodides, Sn^{II}, and oxalic acid.

Quinquevalent neptunium NpO_2^+ is stable in weakly-acid solutions; it disproportionates appreciably in 1 M HCl or $HClO_4$; with increasing acidity the reaction rate

$$2NpO_2^+ + 4H^+ \longrightarrow Np^{4+} + NpO_2^{2+} + 2H_2O$$

increases. Np^V solutions are obtained by heating Np^{IV} in 1 M HNO_3. Complexes of Np^V with oxalate ions are known.

Sexivalent neptunium NpO_2^{2+} is obtained by the action of strong oxidizing agents ($KBrO_3$, Ce^{IV}, etc.) on Np^{IV} and Np^V. In hydrochloric acid it is slowly reduced by the chloride ion, NpO_2^{2+} is very similar to UO_2^{2+} and Pu_2^{2+}, but forms a soluble 8-hydroxyquinolate; its complex with dibenzoylmethane is unstable in water.

Separation Methods

NpO_2^{2+} can be coprecipitated with sodium uranyl acetate; fission products of uranium are removed under these conditions. After reduction with SO_2 on heating, uranium is precipitated by sodium acetate, while Np^{IV} remains in solution. NpO_2^{2+} also remains in solution during precipitation of uranium as the hydroxyquinolate.

NpO_2^{2+} can be precipitated as the double carbonate with sodium.

Np^{4+} is readily coprecipitated with zirconium phosphate or with lanthanum fluoride, under these conditions it is separated from U^{VI}; with zirconium phenylarsonate it is separated from Pu^{III}.

During precipitation of the double sulfate of lanthanum and potassium from a saturated K_2SO_4 solution, neptunium is coprecipitated quantitatively; separation from U^{VI} occurs; Pu^{IV} and Pu^{III} are precipitated with neptunium. After oxidation to NpO_2^{2+}, a repeated precipitation of the potassium-lanthanum sulfate leaves Np in solution (B. V. Kurchatov, V. I. Grebenshchikova, N. B. Chernyavskaya, N. P. Yakovlev, 1955). Np^{4+} is precipitated by sodium benzenesulfinate, while Pu^{3+} remains in solution (L. V. Borisova, 1954).

For separation of neptunium by sorption on resins it is convenient to utilize the single charged ion NpO_2^+. After absorption of UO_2^{2+}, Pu^{IV}, Am^{3+}, and NpO_2^+ on a cation exchanger, the first to be eluted by 1-2 M HNO_3 is neptunium in a radiochemically pure state. Np^{IV} like Pu^{IV}, U^{IV}, and Th is very strongly absorbed from 3 M HCl by cation exchangers; U^{VI} is very readily eluted. In 6 M HCl these elements are eluted in the following sequence: Pu, Np, U, Th. Quinquevalent Np is more readily eluted than Cs^+ even by 3 M HCl. It should be pointed out that resins of the type Dowex-50 reduce Np^{VI} to Np^{V}, and, slowly even to Np^{IV}.

Anion exchange resins are used for the sorption of the chloride complexes of neptunium which are formed under the following conditions: for Np^{VI} at a concentration of HCl > 6M, for Np^{IV} and Np^{V} > 4 M, for Pu^{IV} > 2.5 M for U^{IV} concentrated hydrochloric acid. Pu^{III} and Th are not sorbed. Reduction by iodides in concentrated HCl to Np^{IV} and Pu^{III} allows separation of these on anion exchangers, of the Dowex-1 type.

TABLE 3

Element	Volume of solution	pH	mA/cm^2	Time in minutes
Th	20	2.5	100	120
U	20	2.5	100	120
Np	80	3	250	10
Pu	20	3	100	120
Am	20	3	100	120

Sexivalent neptunium as the nitrate is extracted by ether, etc., under the same conditions as those used for uranyl nitrate F^-, SO_4^{2-}, $H_2PO_4^-$ interfere.

Np^{V} is very poorly extracted from mixtures of the nitrates of NpO_2^{2+} and UO_2^{2+} in ether, neptunium can be eluted by a reducing agent (Fe^{II} + urea).

It is not convenient to extract Np^{IV} as its nitrate for extraction since nitric acid oxidizes it to Np^{V}.

The complex of Np^{IV} with TTA (thiophenecarbonyltrifluoroacetone) is extracted from weakly-acid solutions (0.5 M) together with other ions which have four charges, and with Fe^{III}; separation from Pu^{III} occurs. The complex of Np^{VI} with dibenzoylmethane is unstable; on this basis it is possible to separate uranium from neptunium, since its complex is readily formed and can be extracted by ethyl benzoate.

The electrolytic separation of neptunium, and also that of U and Pu depends on the acidity of the solution and is independent of the anion; for $[H^+] = 10^{-3}$M, Th, U, Np, Pu, and Am can be quantitatively separated from solutions of HNO_3, H_2SO_4, HCl, $HClO_4$, and $H_2C_2O_4$ (A. G. Samartseva, 1956 and 1957). The optimum conditions for 100% separation of amounts of the order of 0.02- 1 γ are given in Table 3.

The appreciable difference in the deposition rate of Np and the other actinoids means that electrolysis can also be used for their separation.

Methods of Determination

The short-lived isotope Np^{239} (half-life period 2.33 days) is measured on the basis of its hard β-radiation: the energy of the β-particles is 0.718 Mev.

The major isotope Np^{237} has a half-life period of 2.20×10^6 years; 1 γ of this isotope in one minute only discharges 1520 α-particles with an energy of 4.77 Mev; consequently, its determination on the basis of an α-count is not suitable – it necessitates careful purification from traces of other α-emmitters, such as Pu, Am, and Cm. In some cases Np^{237} can be determined by isotope dilution using Np^{239}.

It is very difficult to determine Np^{VI} spectrophotometrically, since its absorption in the ultraviolet hardly differs from that of Np^{IV}, while in the visible, absorption is negligible. Np^{V} in 1 M $HClO_4$ is measured at 983 mμ, Np^{IV} at 723 and 964 mμ; Np^{III} has a few absorption bands around 560, 770, and 1000 mμ. The molar absorption coefficients are as follows: Np^{V}, $\alpha_{983} = 295$; Np^{IV}, $\alpha_{723} = 150$, $\alpha_{964} = 190$; Np^{III}, $\alpha_{560} = 45$, $\alpha_{770} = 50$, $\alpha_{1000} = 30$. The bands are displaced slightly in sulfuric acid. For quantitative amounts of neptunium spectrophotometry is still the basic method of determination.

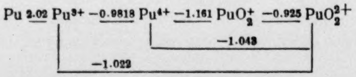
It is probable that analytical methods may be suggested which will be based on reduction and oxidation.

The most likely gravimetric form is the oxide NpO_2 which is stable at 700-800°; it can be obtained by calcining the hydroxide, nitrates, and organic compounds.

It is very likely that color reactions which are known for uranium could be used for the photometric determination of neptunium.

PLUTONIUM

The most stable valence of plutonium in aqueous solutions is 4. The formal potentials of pairs of its ions in 1 M $HClO_4$ at 25° are as follows:



$$Pu \ \underline{2.02}\ Pu^{3+} \ -\underline{0.9818}\ Pu^{4+} \ \underline{-1.161}\ PuO_2^+ \ \underline{-0.925}\ PuO_2^{2+}$$

$$-1.043$$

$$-1.022$$

The potentials change very strongly with the composition of the solutions, the reason, presumably, being the formation of complexes with anions; Pu^{IV} is usually complexed more firmly than Pu^{III} and Pu^{VI}.

The easiest way of preparing Pu^{III} is to dissolve plutonium metal in hydrochloric acid. Reduction of Pu^{IV} and Pu^{VI} to Pu^{III} in acid media by SO_2 is accelerated by heating. Oxidation of Pu^{III} to Pu^{IV} by atmospheric oxygen is considerably slower than in the case of Np^{III}.

Pu^{IV} is obtained by treating strongly-acid solutions with hydrogen peroxide, and also by evaporation with sulfuric acid. This is the most stable oxidized form of plutonium. Pu^{IV} gives stable complexes with HNO_3, $[H_2Pu(NO_3)_6]$, and particularly with sulfates; stable soluble complexes are formed with citric, and tartaric acids, and with Complexone III.

Pu_2^+ is obtained by reduction of PuO_2^{2+}; it is stable only in weakly-acid solutions.

PuO_2^{2+} is obtained by oxidation of lower valence states with chromic acid, persulfate, or permanganate.

Decomposition products of water formed by the action of the characteristic α-radiation of plutonium, reduce Pu^{VI}, Pu^V, and partly reduce Pu^{IV}, while they oxidize Pu^{III}; in 0.5 M HCl the reduction rate amounts to about 0.0035 equivalents/mole Pu in a day.

Methods of Separation

The lanthanum potassium sulfate method described above for Np, is also fully applicable for the separation of plutonium from uranium.

For the separation of natural plutonium from pitchblende, use is made of double precipitation from a nitric acid solution oxidized by heating with $K_2Cr_2O_7$, by twice its volume of a 45% solution of sodium acetate with uranium; under these conditions protoactinium, thorium, and radium are separated; polonium is not removed completely (97 %). The precipitate of the diacetates of uranyl and plutonium are dissolved in nitric acid; after reduction to Pu^{IV} by a double precipitation of sodium uranyl acetate, uranium is separated from plutonium (I. E. Starik, A. P. Ratner, M. A. Pasvik, L. F. Ginsburg, 1957).

Having separated Pu from sodium by precipitation of the hydrate, it is again oxidized to Pu^{IV}, extracted with ether, and, after reduction, coprecipitated with lanthanum fluoride.

For separation from neptunium it is expedient to use the differences in the potentials of the pairs of ions Pu^{III}/Pu^{IV} and $Np^{III}/Np^{IV} = 0.83$ volts. Reduction with hydrazine gives Pu^{III} and Np^{IV}; the latter is precipitated with sodium benzenesulfinate (L V. Borisova, 1954). Use can also be made of differences in the rate of oxidation of Np and Pu to the sexivalent state by 0.1 M $KBrO_3$ in 1 M H_2SO_4: Np is oxidized completely to (VI) in one hour at 35°, and in 7 hours at 20°; Pu at 20° is only oxidized to the extent of 1% after 48 hours; they are separated by precipitating the fluoride PuF_4. In the presence of plutonium the oxidation rate of neptunium increases; presumably, Pu is an oxygen carrier (I. K. Shvetsov, A. M. Vorobyev, 1955).

During oxidation of plutonium in 50% K_2CO_3 solution by ozone or hypochlorite at 95-100°, a green precipitate with the composition $K_4[PuO_2(CO_3)_3]$ is formed; it completely coprecipitates americium which is oxidized under these conditions to Am^V, but hardly traps rare earths at all (G. N. Yakolvev, D. S. Gorbenko-Germanov, 1955).

The solubility of the carbonate complex of Pu^{VI} which is similar to the uranium complex, can be used for many separations.

Precipitation of the oxalates of Pu^{IV} and Pu^{III} in acid media, has been used for separation from UO_2^{2+}, Fe, Mn, Cr, Sr, Nb, etc. (V. V. Fomin, 1956).

Precipitation by hydrogen peroxide, cupferron, and hydroxyquinoline can be used, by analogy with Th and U, for separation from many elements.

Ammonium salicylate (excess) precipitates Pu on heating from solutions with a Ph of 8, in the form of $PuO(Sal')_2$; Pu^{III} at pH 3.5 is precipitated as $Pu(Sal)_3 \cdot 1.5\ H_2O$ (O. E. Zvyagintsev, 1956, 1957).

In extraction separations, plutonium behaves exactly like uranium. Separation of plutonium and uranium is usually based on re-extraction of plutonium by reducing solutions. The use of tributylphosphate for extracting plutonium and other actinoids has been studied by Mckay (1955). The complex of Pu^{IV} with TTA, in contrast to that of U, is extracted by benzene (Irving, 1951).

For sorption methods of separating plutonium see p. 674.

Separation of plutonium from a number of elements can be effected by elution from cation exchangers, or by sorption on anion exchangers of the oxalate complexes of plutonium; in the pH range 1.4-3.0 Pu^{III} forms complexes $[Pu(C_2O_4)_2]^-$, $K'_H = 7.1 \times 10^{-10}$ and $[Pu(HC_2O_4)_4]^-$, $K_H = 1.1 \times 10^{-11}$ (A. D. Gelman, N. N. Motorina, A. I. Moskvin, 1957). In more alkaline media the following complexes are formed $[Pu(C_2O_4)_3]^{3-}$, $K = 2.2 \cdot 10^{-11}$ and $[Pu(C_2O_4)_4]^{5-}$, $K = 2.4 \cdot 10^{-12}$, while for Pu^{IV} the complex $[Pu(C_2O_4)_4]^{4-}$, $K = 3.2 \cdot 10^{-28}$ is formed (V. V. Fomin, S. P. Vorobyev, M. A. Andreeva, 1957).

Separation of plutonium by electrolysis in the form of dense oxide films occurs from alcohol-acetone-water solutions (50 %-45%-5%) at an acidity of 0.1 N and a current density of 40 Ma/cm^2, a deposit density of 0.3 mg/cm^2 in a yield of up to 97% can be obtained. (V. B. Dedov, V. N. Kosyakov, 1955). From less acid aqueous solutions (0.001 N) A. G. Samartseva (1957) obtained 100% separation of plutonium (see p. 675).

Methods of Determination

The most frequently used quantitative method of determining Pu is an α-count. For the isotope Pu^{239} the number of α-emmissions per γ/per minute amounts to 138,000; in preparations subjected to a lengthy irradiation by neutrons, the shorter-lived isotopes Pu^{240} and Pu^{241} are found; under such conditions the counting coefficient changes essentially.

Separate determination of valence states is carried out by spectrophotometric methods. Two absorption bands around 6000 A are used for Pu^{3+}, while two bands at 5000 and 6500 are used for Pu^{4+}, and bands around 8000 A used for Pu_2^{2+}; the latter has the highest molar coefficient. Light absorption of plutonium solutions depends very strongly on complex formation.

The gravimetric form for determination of plutonium is PuO_2, which is obtained by calcining hydrates, nitrates, and organic compounds, at 800-1000°.

A volumetric determination based on oxidation of Pu^{III} to Pu^{VI} by cerium sulfate (IV), using Fe – phenanthroline as indicator has been developed by Kenningheim (1949).

Direct polarographic determinations of PuO_2^{2+} is impossible. Nevertheless, in solutions of potassium oxalate 1 M, at pH 3.5-6, complex plutonium oxalates are formed (IV); at −0.205 volt (saturated calomel electrode) there is obtained a clearly defined wave for a reversible reaction which can be used for quantitative determination (V. V. Fomin, S. P. Vorobyev, M. A. Andreeva, 1957).

Plutonium at a pH of 3-5 gives with Complexone III a stable soluble complex which can be used for titration. Pu^{VI} is reduced under these conditions to Pu^V – and slowly to Pu^{IV} (P. N Palei, O. L. Kabanova, 1956).

AMERICIUM

Americium in reality only exists in three valence states, since Am^{IV} is extremely unstable in aqueous media. The potentials of the ion pairs are as follows:

The chief isotope Am^{241} has a half-life period of only 461.3 years and gives such an intense α-radiation, that in work with quantitative amounts, it is necessary to take into account the intense effect of radiolysis products of water which reduce Am^{V} to Am^{VI}. Complete self-reduction of Am^{V} to Am^{III} at 23° occurs in 66 hours; the reduction rate is linearly dependent on the total concentration, of Am in solution (G. N. Yakovlev, V. N. Kosyakov, 1955), while the rate of reduction of Am^{V} depends on concentration of Am^{V}.

Am^{III} solutions are the end products of self-reduction of Am.

Am^{V} is obtained by oxidation of Am^{III} with ozone in 40-50 % solution of K_2CO_3 at 80-100°.

Am^{VI} is obtained by oxidation with ozone in weakly-acid solutions.

Am^{V} disproportionates in aqueous solutions to give Am^{VI} and Am^{III}; the rate of this reaction in moderately acid solutions (0.1 M H_2SO_4) is negligible, only self-reduction occurs; in 10 M H_2SO_4, $K_D = 3.4 \times 10^4$ liters/meter/hour^{-1}

Am^{V} reacts comparatively slowly with H_2O_2 (A.A. Zaitsev, V.N. Kosyakov, A.G. Rykov, Yu. P. Sobolev, G.N. Yakovlev, 1957).

Am is usually determined on the basis of its α-radiation.

Weighable amounts can be determined on the basis of the light absorption of its solutions. In $HClO_4$ 0.1 M, the molar extinction coefficients are as follows: $Am^{III} - \alpha_{503} = 378$, $\alpha_{811} = 64.4$; $Am^{V} - \alpha_{718} = 59.6$; $Am^{VI} - \alpha_{666} = 24.6$, and $\alpha_{995} = 63.8$. In nitric acid stronger than 3 M and in H_2SO_4 stronger than 10 M the absorption spectra change appreciably.

Am^{III} gives fairly stable complexes with carbonate and acetate ions; in 10% K_2CO_3 solution americium is found wholly in the form of the carbonate complex (G. N. Yakovlev, V. N. Kosyakov, 1955).

Separation of americium by electrolysis, sorption, and by precipitation of the tricarbonate has been mentioned above. It should be noted that there is the possibility of formation of an amalgam of Am during electrolysis (Asprey, 1955). One of the extraction techniques described for separation of Am is extraction of Am-nitrate by means of tributylphosphate (R. I. Brooksbank, et al., 1955).

Curium and the heavier elements have not yet been studied by any methods apart from radiochemical ones.

INORGANIC MICROCHEMICAL ANALYSIS

I. M. Korenman

The methods of microchemical qualitative and quantitative analysis are of great importance for a number of the natural sciences and for production control. They are being increasingly developed in the Soviet Union.

One of the major achievements was the development by N. A. Tananaev (1920) and his school of the method of qualitative spot analysis. Color reactions carried out on filter paper, not only cut down the amount of reagent necessary, but, what is much more important, have made it possible to detect the ions sought in the presence of many other ions without preliminary separation, and have made it possible, by carrying out one reaction, on the basis of the different colors obtained on different parts of a moist spot, to detect immediately two and three ions simultaneously. Noteworthy is the rate with which a spot analysis can be carried out, its simplicity, and the portability of the apparatus. A very important feature of the drop reactions of N. A. Tananaev is their selectivity, their independance of the presence of other ions, as a result of which analysis basically consists in carrying out reactions for separate ions. The spot method has long been in use in factory laboratories, mainly for the analysis of nonferrous metal alloys. The development of new spot reactions has attracted the attention of many Soviet analysts – A. S. Komarovsky, L. M. Kulberg, N. S. Poluetkov, V. I. Kuznetsov, et al.

A further development of spot analysis was its use for colorimetric determinations – spot colorimetry, which was developed by N. A. Tananaev (1929). The intensity of the color of the spot obtained during a spot reaction and the size of the colored zone is related to the concentration of the appropriate ion. When, therefore, the conditions used for carrying out the reaction are standardized, it should be possible to carry out quantitative analysis with a reasonable degree of accuracy, simply and rapidly, using one drop of test solution.

An original and interesting application of the spot method was the use by N. A. Tananaev of the spot method for the quantitative analysis of ferrous and nonferrous alloys in the in situ variant, which has been acknowledged here and abroad. The possibility of carrying out analysis without taking a sample (in this method drops of reagent are placed directly on the metal surface to be tested and observations made on the spot), the simplicity of the method and the speed with which it can be carried out places the in situ method in the rank of important express methods of quantitative microchemical analysis.

Spot analysis has been successfully used for identification of organic compounds (S. I. Burmistrov, I. M. Korenman, L. M. Kulberg, et al.).

An original so-called electrocapillary method of qualitative analysis has been developed by S. I. Dyachkovsky (1931). The method is based on the different rate at which ions move in the surface of a moist filter paper on applying a direct current, as a result of which the ions reach the reagent in a definite sequence, forming with it a number of characteristic colored zones. Since cations and anions move in diametrically opposite directions, it should be possible to detect them simultaneously. The technique of electrocapillary analysis has been developed by N. N. Mironov (1952) and by N. G. Travyansky (1952).

The technique suggested in 1902 by F. M. Flavitsky of carrying out microreactions by a dry method (the trituration method) has been further developed by Soviet analysts. P. M. Isakov (1948) successfully used this method for analyzing minerals. The simplicity of the method the portability of the apparatus, and the possibility of doing without liquid reagents (solutions) has made this method particularly convenient for field laboratories.

Many new reactions, the enumeration of which would occupy a very large amount of space, have been developed by Soviet authors in the field of microcrystalloscopy. A considerable amount of work has been devoted to improving the technique of microchemical experiment (I. P. Alimarin, I. M. Korenman, K. L. Malyarov, et. al.), and to methods of establishing the sensitivity and selectivity of microreactions. An essential step forward in the technique of microcrystalloscopy was the microscope constructed by E. M. Brumberg for work in the ultraviolet; by means of this instrument it is possible to observe the fluorescence of crystals, and to carry out studies by the method of color transformation (Yu. V. Moravchevsky, A. P. Stolyarov).

Noteworthy is the work of O. M. Ansheles and T. N. Burakova (1948, 1950), devoted to the study of the crystallo-optic constants of crystals formed during a reaction, whereby it is possible to carry out an analysis in those cases where as the result of unfavorable conditions of growth, crystals with a noncharacteristic shape are formed. Identification on the basis of the color of crystals can also be carried out by precipitation of mixed crystals, in which the colorless microcomponent is colored by a very small amount of a microcomponent as an impurity (I. M. Korenman, 1932); such reactions are characterized by high sensitivity and specificity.

In recent years the electron microscope has started to find use in microcrystalloscopy (L. I. Zemlyanova and Yu. M. Kushnir, 1952). It can be stated with certainty that the use of the newest methods of investigation will in the immediate future significantly extend the possibilities of microcrystalloscopy.

Semimicro methods already occupy an important place in the practice of factory and educational laboratories. A large part in introducing and developing these methods has been played by I. P. Alimarin, and V. N. Arkhangelsky (1946), V. N. Alekseeva (1952), V. A. Nazarenko and N. S. Poluetkov (1950), E. I. Nikitina (1956), et al.

A lot of interesting work has been carried out by Soviet analysts on the various questions of quantitative microanalysis. Mention must be made of theoretical investigations devoted to the calculation of errors and to increasing the accuracy of quantitative microdeterminations (I. P. Alimarin, 1940; I. M. Korenman, 1936; K. L. Malyarov, 1941; E. A. Shilov, 1926, et al.), and to the development of the techniques and apparatus for work touching upon the concrete determinations of many materials. Sample size, sources of error, and determination and calculation of indicator errors, etc., have been studied in detail. Apparatus constructed by Soviet analysts for quantitative microanalysis is widely used, such apparatus includes: the pneumatic regulator of E. A. Shilov (1926), the hydrostatic buret of M. P. Polyakov (1940), the apparatus of E. A. Andreev and M. B. Neuman (1935) for quantitative microanalysis of gases, etc. Of individual methods mention may be made of microtitration with dye solutions (I. P. Alimarin, 1938, I. M. Korenman, 1935, L. M. Kulberg, 1938, et al.). As a consequence of the high value of the color intensity it is possible to titrate very dilute solutions of dye (0.001 N and less), which leads to high sensitivity and completely satisfactory accuracy. The dye plays the part of titrant and indicator.

The interests of Soviet analysts have extended well beyond the limits of classical microchemical methods (gravimetric and titrimetric). Photometric, gasometric, luminescent, chromatographic, and other methods of analyzing small amounts of materials and low concentrations of materials, have been succesfully developed. It is worth mentioning the method suggested by N. G. Polezhaev (1936) based on a comparison of the intensities of the color of precipitates of mixed crystals, which depends on the concentration of the microcomponent (colorimetry of precipitates). This method has proved particularly useful for determining small amounts of mercury, and has been successfully used for the sanitary-hygienic analysis of air.

Systematic studies on the quantitative microanalysis of minerals have been carried out by I. P. Alimarin and his co-workers (1936); detailed studies have been made of methods for determination of constitutional water, sulfur, ferrous and ferric oxide, total alkali metals, tin, and other elements in minerals and rocks, on the basis of which techniques have been recommended for carrying out microdeterminations which give good results. Quantitative microdeterminations are being used for steel analysis (E. I. Nikitina and A. I. Glazova, 1948).

Qualitative and quantitative ultramicroanalysis has been successfully developed, i.e., analysis of exceptionally small amounts of materials found in very small volumes of test solutions (of the order of cubic millimeters). Using a gravimetric microburet, B. F. Ormont (1929), determined down to $0.25\ \gamma$ of HCl and $0.35\ \gamma$ of As_2O_3 in 1-50 mm^3 of solution with completely satisfactory accuracy. I. M. Korenman and co-workers (1948) have developed apparatus and techniques for titrating 2-50 mm^3 of solution, and also developed a photometric technique for carrying out determinations in equally small volumes of solution, and an apparatus for ultramicro-weighing (1949); techniques and methods of carrying out qualitative reactions with volumes considerably less than 1 mm^3 have also been studied (1952). Particularly noteworthy is the work of I. P. Alimarin and M. N. Petrikov (1952) on the theoretical questions of ultramicroanalysis, the apparatus and techniques of ultramicroanalysis, and ultramicropotentiometry in 0.5–1 mm^3 of solution, by means of which it is possible to determine down to 0.01 γ of material with completely satisfactory accuracy. An original application of ultramicroanalysis can be seen in the work of Yu. G. Titova (1951) – the determination of silver in thin layers deposited by cathodic spraying on glass plates.

In this brief review it is impossible to cover all the work in microchemical analysis. Nevertheless, the examples given demonstrate convincingly that new and original methods of quantitative and qualitative analysis have been developed in the USSR.

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ANNOUNCEMENT

A conference on the application of radioactive isotopes in analytical chemistry, which has been convened by the Chemical Sciences Section of the USSR Academy of Sciences and the Commission on Analytical Chemistry of the Institute of Geochemistry and Analytical Chemistry, will be held on the 2nd to the 4th of December 1957.

The conference will open at 10 a.m. on the 2nd of December in the large hall of the Moscow House of Scientists (Kropotkin Street, 16).

Registration of participants in the conference will be carried out in the Institute of Geochemistry and Analytical Chemistry at the address: Moscow, Vorobevsky Shosse, 47-a, Telephone B-2-05-08, Extension 1-23 and 33.

Organizing Committee

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A STUDY OF THE SYSTEM $BeSO_4 - NaOH - H_2O$ AND ITS ANALYTICAL APPLICATION

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Precipitation of beryllium hydroxide proceeds via formation of a basic salt [1, 2], and separation of the precipitate ceases after addition of an amount of alkali which is less than the stoichiometric amounts [1-3]; when excess alkali is added this hydroxide dissolves, the quantitative aspect of the way these reactions proceed has however not been studied sufficiently. Formation of beryllium hydroxide as an interaction product in a definite system (in which the influence of the anion of the beryllium salt in particular is taken into account) has hardly been investigated at all by the methods of physicochemical analysis. It is, however, just this method which is capable of giving the fullest picture of the formation of beryllium hydroxide, the process of its solution in alkali and other accompanying phenomena.

In the present instance we set ourselves the following problems: 1) to establish the relation between the amount of beryllium which is precipitated and the value of the ratio NaOH : $BeSO_4$ in the original system; 2) to determine the composition of the solid phase at ratios approximating to the stoichiometric ratio; 3) to determine the solubility of $Be(OH)_2$ when there is excess alkali in the system; 4) to test new variants for the analytical separation of beryllium and aluminum by means of alkali.

Test Methods

The system $BeSO_4 - NaOH - H_2O$ was studied by the solubility method. A solution of chemically pure $BeSO_4$ was used, its titer being established by the usual analytical method. It was found that the composition of the salt corresponds to the formula $BeSO_4$.

The solution of sodium hydroxide was prepared with all the precautions necessary to ensure minimum absorption of carbon dioxide.

Mixtures of the appropriate standard solutions were prepared in 100 ml standard flasks, stored in a thermostat at 25°, and mixed by means of a motor operated stirrer. Experiments were carried out in a nitrogen atmosphere in order to avoid absorption of carbon dioxide. The time taken to establish equilibrium was determined experimentally, and was usually found to be two hours. An aliquot of the clear solution (after the precipitate had settled out) was taken for analysis. In all cases the composition of the solid phase was established on the basis of results for the liquid phase of the equilibrium solution. Experiments were carried out for a constant $BeSO_4$ content of the original mixtures equal to 0.025 mole/liter.

Interaction in the System $BeSO_4 - NaOH - H_2O$

The results obtained are given in Table 1 and shown on the diagram; from these results it is clear that no formation of a precipitate occurs in the system until the molar ratio NaOH : $BeSO_4$ in the original mixture exceeds unity. As this ratio increases, the amount of precipitate increases, and, as shown experimentally, at a ratio of NaOH : $BeSO_4$ = 1.8, beryllium cannot be detected in solution either with ammonia or with quinalizarin. Thus, up to the point where sufficient alkali for complete formation of $Be(OH)_2$ has been added, all the beryllium is found in the precipitate, obviously as the basic salt (Table 1, Tests No. 1-6).

$Be(OH)_2$ only starts to dissolve after the accumulation of a certain amount of alkali in the solution [3,4]. In order to establish at what ratio of NaOH : $BeSO_4$ in the original mixture the precipitate, which is completely

TABLE 1

Solubility in the System $BeSO_4-NaOH-H_2O$ at 25° ($BeSO_4$ in the original mixture 0.025 mole/liter)

Experiment no.	$NaOH:BeSO_4$, in the original mixture	Amount of NaOH in the original mixture, in mole/liter	Excess NaOH in the original mixture, in mole/liter	Back titration of NaOH, in mole/liter	NaOH which has reacted, in mole/liter	Be^{2+} content of solution, in g. ions/liter
1	1	0.0250	—	—	0.0250	0.0250
2	1.2	0,0300	—	—	0.0300	0.0223
3	1.4	0.0350	—	—	0.0350	0,0160
4	1.6	0.0400	—	—	0.0400	0.0090
5	1.7	0,0425	—	—	0.0425	0.0058
6	1.8	0.0450	—	—	0.0450	None
7	1.9	0,0475	—	0.0002	0.0473	»
8	2.0	0,0500	—	0.0013	0,0487	»
9	2.1	0,0525	0.0025	0.0040	0,0485	»
10	2.2	0.0550	0.0050	0.0060	0.0490	»
11	2.3	0.0575	0.0075	0.0080	0.0495	»
12	2.4	0,0600	0.0100	—	—	»
13	2.5	0.0625	0.0125	—	—	»
14	2.6	0.0650	0.0150	—	—	»
15	2.8	0.0700	0.0200	—	—	»
16	3.0	0.0750	0.0250	—	—	0.0002
17	3.2	0.0800	0.0300	—	—	0.0005
18	3.59	0.0900	0.0400	—	—	0.0008
19	4.4	0.1100	0.0600	—	—	0.0009
20	4.8	0.1200	0.0700	—	—	0.0026
21	6.0	0,1500	0.1000	—	—	0.0052
22	6.8	0,1700	0.1200	—	—	0.0069
23	8.0	0.2000	0.1500	—	—	0.0098
24	9.2	0.2300	0.1800	—	—	0.0141
25	12.0	0.3000	0.2500	—	—	0.0250

precipitated at a ratio of $NaOH : BeSO_4 = 1.8$, starts to dissolve, a colorimetric method (visual) involving quinalizarin was used. Nevertheless beryllium ions could not be detected in solution up to a value for the ratio of $NaOH : BeSO_4$ in the original solution of 3.0. At this point the concentration of free (excess) NaOH amounted to 0.025 mole/liter. On increasing the amount of alkali in the system further, the amount of beryllium which could be detected in solution increased regularly and, at a ratio of $NaOH : BeSO_4$ in the original mixture of 12.0 (concentration of excess alkali 0.25 mole/liter), all the precipitate dissolved.

Discussion of Results

As can be seen from the solubility diagram (figure), the interaction which occurs in the system $BeSO_4-NaOH-H_2O$ can be represented, on the basis of the results obtained for diluted solutions of $BeSO_4$, as taking place in four stages.

I. Part AB. The value of the ratio $NaOH : BeSO_4$ in the original mixture varies from 0 to 1. Formation of a soluble basic beryllium sulfate occurs

$$2BeSO_4 + 2NaOH \rightarrow (BeOH)_2SO_4 + Na_2SO_4$$

or

$$Be^{2+} + OH^- \rightarrow BeOH^+.$$

II. Part BC. The value of the ratio $NaOH : BeSO_4$ varies from 1.0 to 1.8 (when all the beryllium is already precipitated). The soluble basic salt reacts with sodium hydroxide to form an insoluble basic salt

$$(BeOH)_2SO_4 + 1.6NaOH \rightarrow Be_2(OH)_{3.6}(SO_4)_{0.2} + 0.8Na_2SO_4$$

or

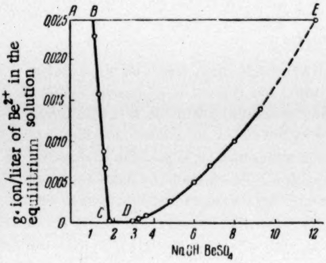
$$5(BeOH)_2SO_4 + 8NaOH \rightarrow 9Be(OH)_2 \cdot BeSO_4 + 4Na_2SO_4.$$

III. Part CD. The ratio NaOH : $BeSO_4$ varies from 1.8 to 2.8. Interaction between sodium hydroxide and the precipitate occurs with gradual substitution of SO_4^{2-} ions in the precipitate by OH^- ions.

IV. Part DE. The ratio NaOH : $BeSO_4$ varies from 2.8 (excess NaOH concentration 0.025 mole/liter) to 12.0 (excess NaOH concentration 0.25 mole/liter); during this stage there is a regular increase in the solubility of beryllium hydroxide in excess sodium hydroxide; this can be represented as follows:

$$Be(OH)_2 + 2NaOH \rightarrow 2H_2O + Na_2BeO_2 \text{ (or } Na_2[Be(OH)_2]).$$

Formation of basic beryllium salts in the system $BeSO_4-NaOH-H_2O$, in the parts of the system corresponding to BC and CD on the diagram, was first of all confirmed qualitatively, and, subsequently, quantitatively as well. The quantitative composition of the precipitate was determined by two methods: 1) by analyzing the equilibrium liquid phase for its content of SO_4^{2-} ions. Since all the beryllium in the corresponding solutions (for ratios of NaOH : $BeSO_4$ of 1.8 and higher) is in the precipitate, then, knowing the SO_4^{2-} content of the original and equilibrium solutions, it is possible to calculate the amount of SO_4^{2-} in the precipitate; 2) on the basis of the alkalinity of the equilibrium solution. If, for a ratio of NaOH : $BeSO_4$ in the original mixture of 1.8, all the beryllium is precipitated, then, on further addition of alkali, the OH^- ions should react with the precipitate and displace SO_4^{2-} ions or partially remain in solution, as a consequence of which the alkaline reaction of the latter should increase earlier than in the case of formation of pure $Be(OH)_2$.



Interaction in the system $BeSO_4-NaOH-H_2O$ ($BeSO_4$ in the original mixture 0.025 mole/liter).

The results for the composition of the precipitate as determined by both methods practically coincided. Thus, by analyzing the liquid phase, the composition of the precipitates was determined for several ratios of NaOH : $BeSO_4$ in the original mixture. In Table 2 is shown how substitution of SO_4^{2-} ions (by OH^- ions) proceeds in the solid phase on increasing the amount of sodium hydroxide in the system (starting at the point where beryllium is completely precipitated).

As can be seen from Table 2, despite the presence of free OH^- ions in solution, SO_4^{2-} ions are trapped by the precipitate and are not completely replaced by OH^- ions even at a ratio of NaOH : $BeSO_4$ in the original mixture somewhat greater than 2.

Determination of precipitate composition when insufficient alkali is present is made difficult as the result of its colloidal properties, nevertheless it can be assumed that the precipitate which is deposited in the system up to a ratio of NaOH : $BeSO_4$ = 1.8 is the basic salt, with a composition $9Be(OH)_2 \cdot BeSO_4$, since the slope of the precipitation line remains constant (see diagram).

TABLE 2

Composition of the Precipitate in the System $BeSO_4-NaOH-H_2O$ at 25°

Experiment no.	Amount taken in solution		SO_4^{2-} found, in g·ions		Composition of the precipitate
	NaOH : $BeSO_4$ in the original mixture	SO_4^{2-}, g·ions	in solution	in the precipitate	
6	1.80	0.00500	0.00450	0.00050	$9\,Be(OH)_2 \cdot BeSO_4$
6a	1.85	0.00500	0.00463	0.00037	$9.25Be(OH)_2 \cdot 0.75BeSO_4$
7	1.90	0.00500	0.00475	0.00025	$9.50Be(OH)_2 \cdot 0.50BeSO_4$
7a	1.95	0.00500	0.00482	0.00018	$9.64Be(OH)_2 \cdot 0.36BeSO_4$
8	2.00	0.00500	0.00484	0.00016	$9.66Be(OH)_2 \cdot 0.34BeSO_4$
9	2.10	0.00500	0.00485	0.00015	$9.70Be(OH)_2 \cdot 0.30BeSO_4$
10	2.20	0.00500	0.00486	0.00014	$9.72Be(OH)_2 \cdot 0.28BeSO_4$

From these results it follows that the behavior of beryllium in the system $BeSO_4 - NaOH - H_2O$ is similar to the behavior of many metals (in analogous systems) which form insoluble hydroxides [5-7], but differs in certain respects. Thus, the fact that all the cation is precipitated before addition of the stoichiometric amount of alkali required, shows that beryllium shows analogies with aluminum [5], gallium [6], thorium, cadmium, and zinc [7]. In its capacity to form soluble basic salts during the first stage of the interaction, beryllium is similar to aluminum, gallium, and thorium, but is not like zinc and cadmium. When excess alkali is present, the amphoteric hydroxide of beryllium behaves like zinc hydroxide, but not like aluminum and gallium hydroxides. This follows from the fact that appreciable solution of $Be(OH)_2$ only takes place when the concentration of the excess alkali exceeds a definite value, while $Al(OH)_3$ and $Ga(OH)_3$ start to dissolve in any small amount of alkali which is in excess of that necessary for forming the hydrate.

The system $BeSO_4 - NaOH - H_2O$ has only been studied for one original concentration of the beryllium salt – and that a small one. At high salt concentrations, in the regions where there is insufficient alkali, one might expect formation of solid phases of another composition. Nevertheless, the process of solution of beryllium hydroxide in alkali should not depend on the original concentration of the beryllium salt. This part of the diagram for the solubility of the system $BeSO_4 - NaOH - H_2O$ (see diagram; part DE) can be regarded, realistically speaking, as the system $BE(OH)_2 - NaOH - H_2O$. Differences in the solubility of aluminum and beryllium hydroxides [5] in alkali served us as a basis for looking for new possibilities of separating aluminum and beryllium by means of sodium hydroxide.

An Alkali Method for Separating Beryllium and Aluminum

The basis of the technique we adopted was the fact that beryllium hydroxide precipitates do not dissolve until the alkali concentration of the solution reaches 0.025 mole/liter, while the amount of aluminum hydroxide which dissolves is equivalent to the amount of alkali taken. Thus, by adding sodium hydroxide to a solution of a mixture of beryllium and aluminum ions until precipitation of the two hydroxides is complete, and then adding more sodium hydroxide until its concentration in the volume taken is 0.02 mole/liter, it is possible to dissolve the aluminum while leaving the beryllium as a precipitate. Under such conditions, the amount of alumunim which can be separated from beryllium will depend on the volume of the solution; for a volume of 250-300 ml, this amounts to 0.15-0.16 g of aluminum.

Results of a series of tests showed that complete separation of beryllium from aluminum by the alkali method is not possible; there are published references which testify to this (without quantitative results). Thus, in one of these tests, mixtures of salts were prepared containing 0.0045 g of beryllium and 0.0848 g of aluminum (Be : Al = 1 : 19) or 0.0125 and 0.1600 g calculated as the corresponding oxides. As a result of separation by the alkali method (the alkali treatment was given twice), 0.0150 and 0.0160 g of BeO were obtained, i.e., 20% more than the amount actually taken. All the same this increase in weight only corresponded to 2% of the aluminum taken. When only one alkali treatment was given this value increased to 5%. Thus, although it is impossible to separate beryllium and aluminum completely by this method, it is still possible to separate most of the aluminum from the beryllium. We should point out that for one treatment with alkali, no loss of beryllium was observed, while a double treatment gave a loss of BeO of the order of 1-1.5 mg.

All that has been said allows one to draw the following conclusion. Complete separation of beryllium and aluminum on the basis of differences in the solubility of their hydroxides in alkali cannot be achieved. Neverthe less, alkali treatment does enable one to obtain (when the conditions noted are observed) all the beryllium hydroxide, containing only a very small amount of aluminum, which can be separated by another method.

The Alkali-Hydroxyquinoline Method of Separating Beryllium and Aluminum

The hydroxyquinoline method suggested by Kolthoff and Sandell [8], as the authors themselves have pointed out, is applicable in those cases where the test solution contains an equal amount of beryllium and aluminum hydroxides, and the amount of each element does not exceed 100 mg.

In connection with what has been said above we suggest therefore a method in which beryllium is separated from aluminum by carrying out a preliminary separation of almost all the aluminum by the alkali treatment. In the residue from the alkali treatment which contains only a small amount of aluminum, beryllium can then be determined by the Kolthoff-Sandell method; by using such a combined method it is possible to deal with samples in which the amount of aluminum in the original material is far greater than that of beryllium.

The experimental procedure is as follows. The test mixture of aluminum and beryllium salts is treated with sodium hydroxide until the red color of phenolphthalein added as an indicator appears (this indicates completion of formation of beryllium and aluminum hydroxides). Excess NaOH is then added to the solution (volume 100-210 ml) on the basis of 1 mole of NaOH per 1 g atom Al, assuming that all the aliquot is pure aluminum, and then more sodium hydroxide is added so that the solution contains 0.01 mole/liter NaOH.

TABLE 3

Determination of Beryllium in the Presence of Aluminum by the Alkali-Hydroxyquinoline Method

Taken, in g					Found, in g	
Be	BeO	Al	Al_2O_3	Al : Be	BeO	error
0.0193	0.0536	0.5130	0.9690	26	0.0542	+0.0006
0.0193	0.0536	0.5130	0.9690	26	0.0540	+0.0004
0.0090	0.0250	0.5155	0.9740	57	0.0262	+0.0012
0.0090	0.0250	0.5155	0.9740	57	0.0238	—0.0012
0.0090	0.0250	0.5155	0.9740	57	0.0244	—0.0006
0.0095	0.0266	1.012	1.91	106	0.0246	—0.0020
0.0095	0.0266	1.012	1.91	106	0.0248	—0.0018

The mixture is kept for 30 minutes and periodically shaken. The precipitate of beryllium hydroxide contaminated with aluminum is filtered off, and washed twice on the filter with water, the precipitate is then washed back off the filter into the original beaker. The precipitate obtained in this way is dissolved in hydrochloric acid, the necessary medium is then prepared and the residual aluminum precipitated with hydroxyquinoline by the usual method [8].

In the course of our work we found that direct precipitation of beryllium with ammonia in the filtrate from the aluminum hydroxyquinolate did not give good results. Consequently it was found necessary to carry out an additional operation of destroying the hydroxyquinolate by means of concentrated HNO_3, after which, precipitation of beryllium with ammonia gave completely satisfactory results.

As the results given in Table 3 show, by using the alkali-hydroxyquinoline method, it is possible to determine small amounts of beryllium in the presence of appreciable amounts of aluminum. Thus, this method can be recommended, for example, for alloys of aluminum and beryllium which contain an appreciably greater amount of aluminum than beryllium. In the work described here we did not study the conditions which would enable one to use this technique in other actual cases, in particular, for the analysis of more complicated alloys. In this given instance we were mainly concerned with the principle of the method. It is proposed to pursue this question further and improve the technique.

SUMMARY

1. Solubility in the system $BeSO_4-NaOH-H_2O$ at 25° has been studied.

2. It has been established that formation of $Be(OH)_2$ proceeds via the formation, first of all, of a soluble basic salt, followed by formation of an insoluble basic salt of variable composition.

3. It has been found that $Be(OH)_2$ starts to dissolve in alkali, only when the concentration of the latter has reached 0.025 mole/liter.

4. A combined alkali-hydroxyquinoline method is suggested for determination of beryllium in the presence of appreciable amounts of aluminum.

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HIGH VOLTAGE ELECTRODIALYSIS

COMMUNICATION 1. SEPARATION OF IMPURITIES FROM SILICIC AND TUNGSTIC ACIDS

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One of the fundamental problems of modern analytical chemistry is the development of methods of separating micro components from the main material for the subsequent quantitative determination of these components. Of interest from this point of view is high voltage electrodialysis, which has been suggested by Kargin and co-workers as a method of purifying various materials and chemical products from impurities [1-4].

During electrodialysis, ionized impurities separate out from solid material dispersed in water or in another solvent, under the influence of a constant electric potential. The dialyzed material (in the form of a finely dispersed precipitate, suspension, sol, or gel) is placed in the middle cell of the dialyzer (Fig. 1), which is separated from the other cells on each side of it by ion-permeable membranes. These end cells are filled with pure solvent or an appropriate solution, and in these cells are immersed the electrodes (usually of platinum or some other electrochemically stable metals). The ions of the impurities, depending on their charge, move under the influence of the field from the middle cell to the electrodes and are thus separated spatially from the precipitate. On applying a small voltage to the electrodes (of the order of one hundred volts) its effect on the transfer of the ions from the middle cell is commensurate with the counter effect of the charge of the membranes with their electrokinetic potential. Under such conditions, ion transfer to the side cells proceeds very slowly or almost not at all [5-8]. This "membrane effect" can be eliminated if the electrodialysis is carried out in a high, constant voltage field (of the order of thousands of volts). Further, it has been found that the efficiency of electrodialysis can be appreciably increased, if use is made of the so-called "ion current" [1]. In this case a solution of a suitable acid or complexing agent is placed in the cathode cell. Such a solution diffuses through the membrane into the middle cell and dissolves the impurity contained in the precipitate. The ions of the impurity are transferred by the current into the cathode or anode cell of the dialyzer, so that it is possible in this way to achieve their complete separation in the shortest possible time.

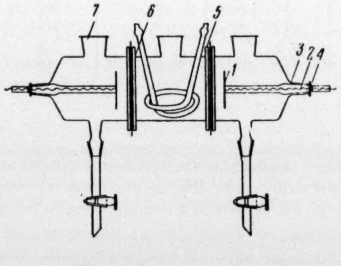

Fig. 1. Electrodialyzer for analytical applications: 1) Platinum disc (electrode); 2) tube with ground joints; 3) inlet for electrodes; 4) grooves for fastening electrodes with rubber rings; 5) end cell; 6) membranes; 7) socket for introduction of V-shaped tube for water cooling.

In the present article a description is given of some results on the separation of impurities in the form of Fe, Cu, Pb, Cd, Sn, Sb, and Bi from SiO_2 and WO_3 by high voltage electrodialysis, using inactive (cellophane) membranes in a three cell dialyzer.

Apparatus

The source of the constant voltage for supplying the electrodialyzer was a high voltage rectifier, constructed on the basis of a double semi-period system with a maximum voltage of up to 2 kilo volts and a maximum current of 350 milliamperes; in some cases a high voltage rectifier with a maximum voltage of 1.5 kilovolts and a maximum current of 0.5 amperes was used. The electrodialyzer which we constructed for analytical use did not contain any parts made from rubber or other plastic materials which would come into contact with the test solutions (Fig. 1).

The contacts of the platinum electrodes (discs) were fused into hollow ground stoppers which were placed in the side cells on the inside.

The membranes 6 were fixed between the well ground sides of the cells 5; all the three cells of the dialyzer were mounted in a horizontal stand.

When, as was the case in some instances, it was necessary to cool the solution in the middle cell, tap water was passed through a coil immersed in this cell, while cooling of the side cells was produced by passing tap water through V-shaped tubes passed through socket 7.

RESULTS AND DISCUSSION OF RESULTS

1. Removal of Impurities from Silicic Acid

Silicid acid hydrogel possesses a considerable absorption capacity; in a pure state it absorbs the ions of practically all the metals, particularly iron, aluminum, and copper.

The ions of these metals are firmly held by silicic acid and their complete removal by washing with acids and water is practically impossible.

a) Removal of Impurities in the Form of Fe and Cu

5 g of finely ground SiO_2 powder (chemically pure grade) was wetted in a platinum basin with 25 ml of 1 N HCl and 10 ml of $Fe(NO_3)_3$ solution containing 0.098 mg Fe/ml. The amount of iron added was 0.02% of the weight of SiO_2 taken. The contents of the basin were carefully mixed and evaporated to dryness on a water bath, after which they were quantitatively transferred to the middle cell of the dialyzer. A solution of HCl or HNO_3 0.05 N and higher, was added in small portions (0.5-1 ml) to the cathode cell and twice-distilled water was added to the anode cell. The stirrer was then lowered into position and the high voltage switched on. After every 30 minute period the solutions in the side cells were poured off, and the cathode and anode cells filled up again with fresh acid of the concentration indicated, and twice-distilled water respectively; electrodialysis was then continued until a small current was established (5 milliamperes). The solutions poured out of the side cells were evaporated to small volume (about 15 ml) and poured into a standard 50 ml flask.

TABLE 1

Electrodialysis of SiO_2 Gel Containing Traces of Iron (2×10^{-2}%)

Aliquot, in g	SiO_2 introduced, in mg	Fe as % of SiO_2	Voltage,* in volts	Current, ** in milliamps	Time of electrodialysis, in hours	Fe removed, in mg**
5	0.98	0.02	1000	10	6	1.0
5	0.98	0.02	1000	10	9	0.9
5	0.98	0.02	900	10	9	1.0
5	0.98	0.02	1100	8	7	1.0
5	0.98	0.02	1100	10	8	0.9

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* Determined by the thiocyanate method [13].

** At the end of the experiment.

Into this same flask were poured solutions obtained by a triple treatment of the platinum electrodes with nitric acid (1 : 1) and water, since it was established in preliminary experiments that the impurities removed from the middle cell are electrolytically precipitated (partially) on the cathode or anode according to the nature of the impurities.

Table 1 contains the results obtained during separation of impurities from a gel of silicic acid.

In another series of our experiments, samples of SiO_2 with an initial content of 5×10^{-3}% of Fe and Cu were subjected to electrodialysis by the technique described. The content of these impurities in the SiO_2 was determined spectrographically before and after electrodialysis. For this purpose the ISP-22 quartz spectrograph was used, in conjunction with reproduction iso-orthochromatic plates with a sensitivity of 1.4 GOST units. The test sample was evaporated from the cavity of a carbon electrode at a constant current of 10 amperes. The lines used were the most sensitive lines for these elements: Fe – 3020.6, Cu – 3274.0 A.

During these experiments it was established that separation of hundredths of a percent of Fe and Cu can be achieved in 6-9 hours on using the "ion current" method. Removal of thousandths of a percent of Fe takes a longer time (10-15 hours), under conditions where the dialyzed samples are given a preliminary treatment with acid, and excess of the latter is removed by evaporation on a water bath.

We should like to point out that Matveeva [1] has already established previously that it is possible to remove small amounts of iron, copper, and some other metals from SiO_2 by means of electrodialysis.

b) Removal of Traces of Pb, Cd, Bi, Sn, and Sb from SiO_2

1 g of SiO_2 (chemically pure grade) was placed in a beaker and dissolved on heating in 10 ml of 10% NaOH. To this solution was added 1 ml each of standard solutions of the nitrate or chlorides of the metals indicated above (1 ml of each solution contained 1 mg of metal), and 3 ml of HCl (1.19). The precipitated gel of silicic acid was washed with distilled water by decantation, and was then placed in the middle cell of the dialyzer. The cells were initially filled with twice-distilled water and electrodialysis continued until a current of 5-10 milliamperes, and a maximum voltage were established, in order to remove NaCl and HCl adsorbed by the gel.

Next, the cathode cell was filled with a dilute solution of HCl, HNO_3 or $C_4H_6O_6$ (in certain cases, mixtures of these acids), and electrodialysis carried out for several hours, in the course of which the acid in the cathode cell and the distilled water in the anode cell were changed every 30 minutes. The experiment was terminated when the current reached its minimum value and the voltage its maximum value accordingly. Spectrographic analysis of SiO_2 samples was carried out using the most sensitive lines: Sb – 2598.1 A, Pb – 2833.1 A, Sn – 2840.0 A, Bi – 3067.7 A, Cd – 3261.1 A. As a result of these experiments it was established that removal of Pb, Cd, and Bi at contents of these elements ranging from 1×10^{-1} to 5×10^{-2}% was quantitative after 7-9 hours, when the method involving the current of Cl^-, NO_3^-, $C_4H_6O_6^+$ was used, the cathode cell being filled with dilute solutions of the appropriate acids or their mixtures. For the same initial percentage content of Sn and Sb in SiO_2, their content decreased by one order (1×10^{-2}).

2. Removal of Traces of Pb, Cd, Sn, Sb, and Bi from Tungstic Acid

Test samples containing the metals indicated as impurities were prepared as follows. An aliquot of ammonium tungstate (1 g or 0.733 g of the salt corresponding to 0.873 or 0.640 g WO_3) was dissolved in 20 ml of twice-distilled water. To this solution was added either singly, in pairs, or altogether, Pb, Sn, Cd, Bi, and Sn as impurities in the form of exactly measured volumes of solutions of their nitrates or chlorides, the amounts ranging from 0.5 to 0.02 mg, which, expressed as a percentage of the WO_3 taken, corresponded to 5.7×10^{-2} and 3.1×10^{-3}%. Tungstic acid was then precipitated with HCl (2 ml of 1 : 1), and dried on a sand bath; it was finally calcined in a muffle at 600° to form WO_3 with an orange color.* The oxide was quantitatively transferred to the middle cell of the dialyzer filled with twice-distilled water, the cathode cell was filled with a dilute solution of one of the acids (0.1 N HCl, HNO_3, $C_4H_6O_6$, H_2SO_4, H_3PO_4), or in some cases with their mixtures.

During electrodialysis the solutions from the anode and cathode cells were periodically poured off at the end of each 30 minute period, and the cells filled with distilled water. The solutions which had been poured off were concentrated by evaporation, and their content of Pb, Cd, Bi, and Sb determined colorimetrically by Sandell's method [13]; the precipitate from the middle cell was analyzed spectrographically after drying it.

The analytical lines listed above were used for the spectrographic determination of Sb, Pb, Sn, Bi, and Cd in tungstic acid. During analysis the carbon electrode was packed half full with test sample and carbon powder strewn over the latter. Good separation of Sb, Pb, Sn, Bi and Cd from W was observed with time.

As a result of these experiments, we found that lead and cadmium present as impurities in WO_3 could be separated quantitatively from the latter, on an average, in the course of 9 hours, when the following conditions were observed: a) when the solutions in the side cells were renewed periodically; b) when the current of the ions Cl^-, NO_3^-, and SO_4^{2-} was used. The content of Bi, Sb, and Sn present as impurities decreased by one order as a result of electrodialysis under these conditions. When all three cells of the dialyzer were filled with concentrated acetic acid, antimony was removed quantitatively from WO_3, while the content of Sn decreased by one order. This result indicated the effect of the high voltage gradient on removal of the impurity. Antimony compounds hydrolyze readily in not too concentrated solutions of mineral acids, and readily dissolve in glacial acetic acid to form solutions with low electrical conductivity.

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* The calcined oxide WO_3, in contrast to the moist form, is practically insoluble during electrolysis.

3. The Factors Which Influence Removal of Impurities

a) Solubility of the Isolated Impurities

Traces of metals in the form of any compound can only be removed from the main component when these compounds form a true solution, and positive or negative ions are formed during electrodialysis.

A necessary condition for this to occur is the high solubility of the impurity to be removed as compared with the solubility of the main component.

To this is related the fact that the first analytical applications of electrodialysis were confined to removal of the alkali and alkaline earth metals serving as impurities, which do not hydrolyze in the pH range close to neutral [9, 10]. In such cases it proved possible to apply comparatively low constant voltages to the electrodes (of the order of hundreds of volts).

According to our results, Pb and Cd as impurities can be quantitatively removed from SiO_2 and WO_3 (the pH at the point where these metals start to precipitate lies within the range 5-7).* More difficult (in the sense that it takes longer) is removal of Fe as an impurity (pH at the commencement of precipitation is 3). Sn, Sb, and Bi are not completely removed when using the current of the ions of dilute solutions of mineral acids.

This is related to the insignificant solubility of the hydroxides of these metals, which are readily formed as a result of hydrolysis in weakly acid solutions. It would seem that hydrolysis of the ions of these metals might be suppressed by increasing the acidity of the solution. Tests carried out with the ion current when the cathode cell was filled with 0.1 N (and higher) acid solutions (HCl, HNO_3), however, did not give positive results. The reason for this is as follows.

Excess of another electrolyte, for example, acid, lowers the efficiency of electrodialysis, rendering it extremely slow. In actual fact, the transport number t_i of ions of the i'th type in a solution with n different types of ions is determined by the relation:

$$t_i = \frac{q_i}{Q} = \frac{c_i z_i u_i}{\sum\limits_{i=1}^{n} c_i z_i u_i},$$

where c_i is the concentration (g·equivalents/liter) of an ion of the i'th type, and z_i, u_i are the charge and mobility of this ion respectively [11].

It is obvious from this equation that the fraction of the current carried by ions of the i'th type will fall with increasing concentration of ions of other types. Consequently, during electrodialysis of a solution containing excess of another electrolyte, the main part of the current will be expended in carrying the ions of this electrolyte. The conductivity of such a solution is high, and the potential drop in it, in accordance with Ohm's law, is insignificant. Under such conditions desorption of ionized impurities from the surface of particles of the suspension hardly proceeds at all. As a result of electrodialysis, the excess acid in the middle cell is removed, and the pH reaches the value at which the hydroxides, of the dialyzed metals (in our case Sn, Sb) are precipitated, which, as stated above, are not completely removed because of their insignificant solubility.

b) Effect of Back Diffusion of Electrolyte from the Side Cells

As pointed out above, when there is an appreciable excess of acid in the solution being dialyzed, removal of the ions of the impurity is practically impossible. We studied the rate at which acid is removed from the middle cell by the electrical conductivity method.

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* The pH at the commencement of precipitation is not a strictly defined value since it depends on the method used for measuring it. It can vary with the concentration of the ions to be precipitated, with the presence of complexing agents, temperature, and other factors.

The specific conductivity of HCl solutions in the middle cell was measured by means of an apparatus constructed by GEOKhI of the USSR Academy of Sciences and Factory No. 4106 [12]. Test samples of the solutions in the middle cell were transferred to a cell for measuring the electrical conductivity; the cell was fitted with platinized platinum electrodes; the cell constant was 0.386. The middle cell of the dialyzer was filled with 25 ml of 0.2 N HCl; the interelectrode distance was 8 cm, while the area of each electrode was 1.5 cm^2. The voltage applied to the dialyzer electrodes initially was 20 volts at a current strength of 0.3 amperes, while at the end of the test the voltage was increased to 1800 volts, and the current dropped to 20-30 milliamperes. Electrodialysis was carried out without agitation. At the end of every 10 minute period, the solutions from the anode and cathode cells were poured off, and the cells filled up again with twice-distilled water ($\chi = 3.8 \times \times 10^{-6}$ ohm^{-1} cm^{-1}), while, at the same time, the electrical conductivity of the solution from the middle cell was measured.

Removal of acid from the middle cell of the dialyzer proceeds fairly slowly; establishment of a constant value for the electrical conductivity of 5.5×10^{-4} $ohm^{-1}cm^{-1}$ (corresponding to 6×10^{-4}N HCl) took 310 minutes; consequently, dialysis of acid was still incomplete after this time (Fig. 2).

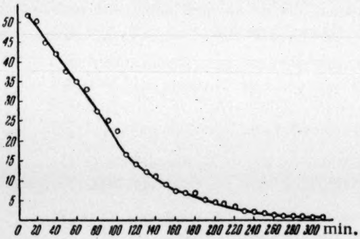


Fig. 2. Change in the electrical conductivity of the HCl solution in the middle cell with time. Initial HCl concentration 0.2 N, final concentration 6×10^{-4}N. Values of $\chi \cdot 10^3$ $ohm^{-1}cm^{-1}$ are plotted along the ordinate.

On Fig. 3 is shown the electrical conductivity curve of the solution in the middle cell, for the case where the latter was filled before the test with twice distilled water, while the cathode cell contained a HCl solution with an initial concentration of 0.1 N, and the solution from the anode cell was poured off every 20 minutes and replaced with twice-distilled water.

The presence of a maximum on the curve in the given instance is connected with the effect of two counteracting factors: diffusion of dissolved HCl into the middle cell from the cathode cell, and the transport of ions of acid from the middle cell under the effect of the field in the solution.

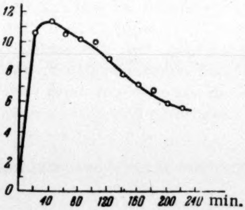


Fig. 3. Changes in the electrical conductivity of the solution in the middle cell, filled initially with twice-distilled water, the cathode cell being filled with 0.1 N HCl. Values of $\chi \cdot 10^3$ $ohm^{-1}cm^{-1}$ are plotted along the ordinate.

On Fig. 4 is shown the electrical conductivity curve of the solution in the middle cell, for the case where the cathode cell is filled with 0.1 N HCl, while the solution in the anode cell is not changed. At the start of the experiment the electrical conductivity increased fairly rapidly as a result of diffusion of HCl; subsequently it tended to reach a constant value which is determined by the equilibrium concentration of the acid in these cells of the dialyzer.

Such a set of conditions is the least favorable for removal of impurities from the middle cell.

It can be concluded from these experiments that the efficiency of electrodialysis will be enhanced by shifting the equilibrium concentrations to the middle and side cells. This change of solvent in the ideal case would be a continuous process, since, in such a case, the effect of the back diffusion from the side cell into the middle cell would tend to a minimum. It has been shown that such a state of affairs can be realized by carrying out the electrodialysis in a five cell electrodialyzer [1].

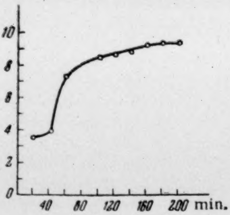


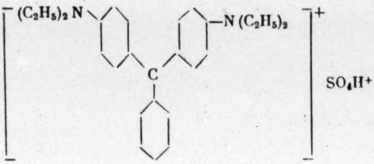
Fig. 4. Electrodialysis of 0.1 N HCl from the middle cell without changing the solution from the anode cell; the cathode cell is filled with 0.1 N HCl. Values of $\chi \cdot 10^3\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$ are plotted along the ordinate.

c) Effect of the Nature of the Bonds Between the Impurity and the Main Component

The rate and completeness of removal of impurity, all other conditions being the same, depend on the nature of the bond between the impurity and the main component. When the impurity enters into the composition of the crystalline lattice of the precipitate, its quantitative removal is difficult, or practically impossible. Desorption of the ions of the impurity from the surface of an amorphous insoluble precipitate proceeds more fully.

All factors which lead to a deterioration of the adsorption of ions of the impurity on amorphous precipitates, increase the completeness of its removal during electrodialysis. For example, it is known that the presence of surface active dyes in the solution prevents coprecipitation of certain Group III metals with sulfides of the hydrogen sulfide group of metals.

We assumed that the presence of a cation active dye in solution during precipitation of a gel of silicic acid from this solution would decrease coprecipitation of impurities, and would speed up their dialysis. In our experiments we used Brilliant Green which has the formula given below, as a cation active dye



An aliquot of SiO_2 (1.5 g) was dissolved in 10 ml of 10% NaOH by heating in a platinum crucible. To this solution was added an aqueous or alcoholic solution of the dye (0.2 g in 25 ml of solvent), and 6 ml of HCl (1 : 1) for precipitating the gel of silicic acid.

The gel which separated out was washed several times with twice-distilled water, and, after getting a negative reaction for Cl^-, was transferred to the middle cell of the dialyzer filled with twice-distilled water. Electrodialysis was carried out over a period of 5 hours. Initially, electrodialysis was carried out using the ion current (the cathode cell was filled with dilute HCl), and subsequently with a continuous flow of twice-distilled water through the side cells.

Spectrographic analysis of the dialyzed samples of SiO_2 to which dye had been added, showed that iron as an impurity was removed practically quantitatively under these conditions.

It should be pointed out that removal of iron is not simply a case of washing out its ions from the SiO_2 gel by decantation. SiO_2 samples prepared by the technique described above, but not subjected to electrodialysis, showed practically no change in their iron content as compared with the original samples.

In conclusion, we should like to thank V. A. Kargin, and D. I. Ryabchikov for their constant interest in the work and for their cooperation in carrying it out.

SUMMARY

1. By means of high voltage electrodialysis using cellophane membranes, it has been shown that it is possible to remove traces of Fe, Cu, Pb, and Cd quantitatively (hundredths and thousandths parts of one per cent) from SiO_2. Complete removal of Bi, Sn, and Sb was not achieved, their concentration was decreased by one order.

2. During electrodialysis of tungstic acid containing 5×10^{-2}-3×10^{-3}% of Pb, Cd, Bi, Sn, and Sb, traces of Pb and Cd were removed quantitatively, while the content of Sn, Sb, and Bi decreased by one order. Quantitative removal of Sn and Sb from WO_3 is possible on carrying out electrodialysis in concentrated acetic acid.

3. Incomplete removal of Sn, Sb, and Bi from WO_3 is connected with the high tendency of compounds of these elements to hydrolyze in aqueous solutions with a low acid concentration.

4. Excess of another electrolyte in the dialyzed solution, and also accumulation of isolated impurities in the side cells of the dialyzer, lower the efficiency of dialysis, and increase its duration.

5. Complete removal of impurities by electrodialysis, other conditions being equal, depends on the nature of the bond between the impurity and the dialyzed precipitate, and on the structure of the latter.

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* In Russian.

** Russian translation.

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ISOTOPE DILUTION TECHNIQUE

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Until recently determination by the isotope dilution technique has been mainly applied in organic chemistry, biochemistry, and medicine, and only comparatively recently inorganic chemistry. This technique allows one, even when the test element has not been completely isolated, to determine it quantitatively; this is very important in the case of elements for which there are no satisfactory quantitative methods of determination. A known amount of the radioactive isotope of the element to be determined is added to the test solution, the specific activity of this isotope being known. Subsequently the specific intensity of the compound of the test element which has been isolated is determined. From the degree of dilution of the radioactive isotope, it is possible to assess the amount of the element in the test mixture. The content of the element is determined by the following equations:

$$W_2 = W_3 \frac{A_1}{A_3} \tag{1}$$

and

$$W_2 = W_1 \left(\frac{S_1}{S_2} - 1 \right), \tag{2}$$

where W_2 is the sought for amount of test element; W_1 is the amount of the element introduced with the radioactive isotope; W_3 is the amount of element isolated; A_1 is the activity introduced (in impulses/minute); A_3 is the activity of the compound isolated (in impulses/minute); S_1 is the specific activity of the radioactive isotope $\frac{\text{(impulses/minute)}}{\text{mg}}$; S_2 is the specific activity after dilution $\frac{\text{(impulses/minute)}}{\text{mg}}$.

Formula 1 is applied when radioactive isotopes are used without a carrier; when the indicator contains a weighed amount of radioisotope, formula 2 is employed.

The variants of the method, their possibilities, advantages and disadvantages have already been described [1].

The present article contains experimental data on the technique and operational procedure when isotope dilution is used.

Preparation of Pure Radioactive Isotopes

The radioactive indicators used were Bi^{210} (RaE) with a half-life period of T = 5.02 days, and E = 1.17 Mev; and Pb^{212} (ThB) with a half-life period of 10.6 hours and E = 0.355 and 0.589 Mev. Radium E was removed from RaD, found with it in equilibrium, by internal electrolysis [2] from a 3-5% acetic acid solution at 80-85° over a period of 40 minutes. The cathode was a platinum grid cylinder, while the anode was a lead plate.

Thorium B was obtained from the active deposit of thoron which had accumulated on a Pt grid, connected with the negative pole of a gB battery (2 batteries), with a total potential of 300 volts. The anode was a copper wire.

Radiothorium was used as the emanating preparation. After keeping for 2-3 days, the active deposit was removed with nitric acid to give an indicator with a high specific activity [3,4]. The isolated radioisotopes were checked for their radiochemical purity by means of their β-radiation and half-life periods.

Experimental Technique

The effects of various factors on the accuracy of the isotope dilution method, such as the yield of test element, its content in the test sample, the ratios of the amounts of test element and indicator in test solutions, etc. were studied on the basis of the precipitation of bismuth and lead by inorganic and organic reagents.

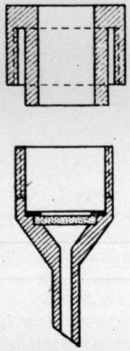

Fig. 1. Filtering funnel with glass filter.

Bismuth was determined as the phosphate and pyrogallate [5]. In addition, bismuth and lead were determined by a new method, based on the precipitation of these elements as their benzenesulfinates [6, 7]. Bismuth and lead form compounds with a constant composition with these reagents; furthermore, by regulating the pH it is possible to alter the completeness of precipitation of these elements.

The phosphate method did not give satisfactory results. The error was 10-15%. We found that the reason for this was that the precipitate of bismuth phosphate did not always correspond to the composition indicated by its formula.

Bismuth was precipitated as pyrogallate as follows. To a nitric acid solution of bismuth containing approximately 1 mg/ml, was added indicator RaE with an activity of 4000-6000 impulses/minute. After addition of a saturated solution of pyrogallol, the precipitate was transferred onto weighed porous glass discs fastened in a filtering apparatus made from plexiglass (Fig. 1). The precipitate was washed and dried at 110°; it was then weighed and its activity measured on a TM-20 torsion counter. Knowing the initial specific activity of the indicator, and the specific activity of the compound isolated, then, by using formula 1 or 2, the required amount of element can be calculated.

We developed the following technique for precipitation of bismuth and lead as the benzenesulfinates. To a nitric acid solution of bismuth and lead was added a known amount of nitric acid, until its concentration in solution was 0.3 N in the case of lead, and 0.5 N for bismuth. At such HNO_3 concentrations, the yield of lead amounted to 50-60%, while that of bismuth was 70-75%. Solutions of the indicators RaE and ThB, usually in amounts of 0.1-0.15 ml, were measured from micro pipets connected to a syringe, the movement of whose plunger was governed by a microscrew.

Precipitation was carried out with a 40% solution of ammonium benzenesulfinate at room temperature. These precipitates were also filtered through porous glass discs, washed with a 0.1% solution of the reagent acidified with HNO_3, and then washed with ether and dried at 80° (bismuth benzenesulfinate), and 120° (lead benzenesulfinate) respectively; finally, the activity was measured. Bismuth and lead are not precipitated quantitatively by this reagent; the composition of the precipitates corresponds accurately to the formulas $Bi(C_6H_5SO_2)_3$ and $Pb(C_6H_5SO_2)_2$. In this respect, therefore, the isotope dilution method is fully applicable.

Technique of Radiometric Measurements

Determination by the isotope dilution technique includes measurement of the activity of the preparation isolated as well as weighing it.

The best accuracy for relative measurement was obtained by using porous glass discs 12-15 mm in diameter and 4 mm thick for filtration; they maintain a constant weight well; the precipitate of the preparation to be measured was uniformly distributed on the filter surface on sucking the filtrate through with a water pump.

The setup on which the preparation was placed for making activity measurements was centered so that the geometrical conditions of the counter were always the same.

During measurements of samples differing in weight, it was necessary to take into account the change in the counter rate with the weights of the preparations being measured.

We constructed self-scattering (Fig. 2) and self-absorption curves (Fig. 3) for RaE with E = 1.17 Mev, and for ThB with E = 0.355 and 0.589 Mev.

Samples containing varying amounts of carrier were compared with standard samples of equal activity but free from carrier. These curves show, on the one hand, the effect of the uniformity of distribution of the

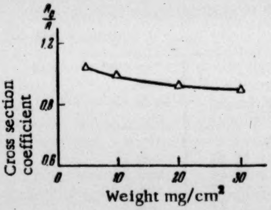

Fig. 2. Relation between self-scattering and weight of source for RaE.

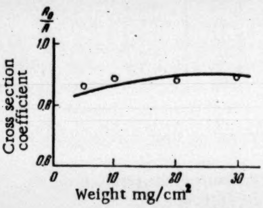

Fig. 3. Relation between self-absorption and weight of source for ThB.

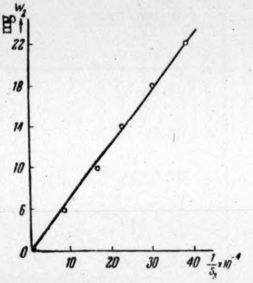

Fig. 4. Calibration curve for the relation between weight of isolated precipitate and specific activity.

precipitate on the change in activity of the samples; while on the other hand, they show that for a high radiation energy (Bi^{210}), an increase in activity with increasing weight of the source is obtained as a result of self-scattering (Fig. 2). For a low radiation energy (Pb^{212}), a decrease in activity with increasing weight of the source as a result of self-absorption predominates (Fig. 3).

In order to avoid errors arising from these factors, it is necessary to have complete identity in the preparation and measurement of standards and samples. In this connection, the reference standards were prepared as follows:

1) In cases where the amount sought was to be determined by calculation, a known amount of indicator (0.1 ml) was measured onto discs of tracing paper with a diameter of 12-15 mm with varying amounts of carrier, and dried under an infra-red lamp; the discs of tracing paper were then fixed on to the porous glass discs and measurements of activity carried out.

2) When the amount sought was to be determined graphically, calibration curves were drawn; this was carried out by adding the same amount of indicator solution to solutions containing various amounts of test element; precipitation was then carried out by the same technique as that used for the test samples (Fig. 4).

After drying, the precipitates were weighed and their activity measured on a counter. On the basis of these results the specific activity of the samples isolated was calculated in impulses/minute/mg. Calibration curves of W_1 against $1/S_2$ were constructed according to the equation:

$$W_2 = A_1\left(\frac{1}{S_2}\right) - W_1, \qquad (3)$$

where W_2 is the amount of element determined in milligrams; W_1 is the amount of element introduced with the radioactive isotope; A_1 is the activity introduced with the radioactive isotope (impulses/minute); S_2 is the specific activity of the isolated sample (impulses/minute/mg).

Using this graph, and knowing the specific activity, it is possible to determine the original amount of element.

Relation Between the Accuracy of the Method and the Content of the Element in the Original Sample

In order to establish the effect of the original amounts of the element on the accuracy of the isotope dilution method, various amounts of test element were taken ranging from 1 to 20 mg, and precipitation and measurements of activity carried out by the procedures described above. The results obtained are given in Table 1.

In experiments Nos. 1, 2, 7, 8, and 15, bismuth was isolated by the pyrogallol method. In all the remaining experiments bismuth was isolated as the benzenesulfinate.

It is evident from Table 1 that the best results are obtained when working with amounts of 8-10 mg. For amounts less than 5 mg the error is 5-10%; it is not convenient to work with amounts greater than 20 mg because of the large weight, while the accuracy drops because of a decrease in specific activity as will be shown below.

TABLE 1

Experiment number	Bi taken, in mg	Bi found, in mg (W_2)	Activity introduced with indicator, imp/min (A_1)	Activity of isolated compound, imp/min (A_2)	Calc. amount of Bi, in mg (W_2)	Error, in %
1	17.35	17.15	6913	6870	17.23	—0.7
2	17.35	16.95	6913	6825	17.09	—1.5
3	16.92	11.09	7274	4690	17.17	+1.5
4	16.92	6.26	7274	2618	17.27	+2.1
5	16.92	9.54	7274	4220	16.48	—2.6
6	16.92	8.33	7274	3362	16.57	—2.05
7	8.57	8.57	6987	6984	8.57	0
8	8.57	8.72	6987	7070	8.85	—2.8
9	8.46	5.54	3625	2322	8.65	+2.2
10	8.46	5.50	3625	2290	8.73	+3.2
11	8.46	6.14	3625	2685	8.3	—1.9
12	8.46	5.23	3625	2165	8.77	+3.7
13	4.23	2.37	1778	914	4.62	+9.2
14	4.23	1.8	1778	703	4.56	+7.8
15	1.74	1.36	6913	5007	1.85	+6.6

Relation Between the Accuracy of the Method and the Specific Activity of the Isolated Compound

Determination of the amounts sought was determined graphically. On the basis of the results given in Table 2 a calibration curve was drawn relating W_2 to $1/S_2$; this is represented on Fig. 4.

TABLE 2

Pb taken, in mg (W_2)	Specific activity of the isolated compound, in S_2 $\frac{\text{impulses/minute}}{\text{mg}}$	S_2, reference	$1/S_2$ in $\frac{\text{impulses/minute}}{\text{mg}}$
6	1103 1176	1139	$8.78 \cdot 10^{-4}$
10	580 611	590	$16.95 \cdot 10^{-4}$
14	432 445	438	$22.8 \cdot 10^{-4}$
18	317 330	323	$30.9 \cdot 10^{-4}$
22	263 245	254	$39.4 \cdot 10^{-4}$

TABLE 3

Pb taken, in mg	Specific activity of the isolated compound, in S_2 $\frac{\text{impulses/minute}}{\text{mg}}$	$\frac{1}{S_2}$ in $\frac{\text{impulses/minute}}{\text{mg}}$	W_2	Error, in %
7.30	981	$10.4 \cdot 10^{-4}$	7.2	—1.23
8.04	819	$12.2 \cdot 10^{-4}$	8.0	—0.45
11.28	521	$19.4 \cdot 10^{-4}$	11.6	+2.8
14.69	388	$25.8 \cdot 10^{-4}$	14.9	+1.4
18.74	302	$31.8 \cdot 10^{-4}$	17.9	—4.7
17.68	299	$33.4 \cdot 10^{-4}$	18.7	+6.3
19.10	270	$37.1 \cdot 10^{-4}$	20.5	+6.9

The range of concentrations of the element was selected according to what it was intended to determine in the test solution.

Lead was precipitated as the benzenesulfinate according to the technique described above.

To test solutions containing various amounts of lead (from 6 to 22 mg) was added the same amount of radioactive isotope. After measuring the specific activity of the precipitates isolated, the amount of element was determined. Results of such determinations are given in Table 3.

From these results, it is evident that with decreasing specific activity of the isolated compound, the accuracy of the method drops. In order to ensure sufficient accuracy, it is desirable to work with a specific activity of not less than 400 impulses/minute/mg.

Relation Between the Accuracy of the Method and the Ratio of the Amounts of Test Element and Indicator

Indicators with the requisite specific activity were prepared by adding various amounts of inactive carrier in the form of a nitric acid solution to the radioactive isotope of bismuth Bi^{210} without carrier, prepared as described above. The indicator was then added to the test solution in such amount that the ratio of the amount of element taken with the indicator, to the amount of element contained in the original solution, was 1 : 5, 1 : 2, and 1 : 1. Bismuth was precipitated as the pyrogallate.

The results obtained are given in Table 4.

TABLE 4

$W_1 : W_2$	Bi taken, in mg		Bi + Bi* obtained, in mg	Initial specific activity S_1, in impulses/min / mg	Final specific activity S_2, in impulses/min / mg	Sought for amount of Bi calc. value $W_2 - W_1 \left(\frac{S_1}{S_2} - 1\right)$	Error, in %
	W_1	W_2					
1 : 5	1.69	8.46	8.97	3190	535	8,37	1.1
	1.69	8.46	8,98	3190	532	8.44	0.25
1 : 2	3,38	6.77	8.62	1735	589	6.61	2.4
	3.38	6.77	8.63	1735	584	6.66	1.6
1 : 1	5.08	5.08	8.89	1670	887	4.48	11.8
	5.08	5.08	8.65	1670	797	5.54	9.2

It is quite obvious that the optimum ratio of the amount of indicator to test element $W_1 : W_2$ is equal to 1 : 5.

The ratio $W_1 : W_2$ primarily determined the degree of dilution of the indicator; the greater the difference between the specific activity of the indicator S_1, and the specific activity after dilution S_2, the higher the experimental accuracy.

Accordingly, S_2 should not be less than 400 impulses/minute/mg, while this, in turn, will require the use of an indicator with sufficiently high specific activity S_1. Under such conditions, the accuracy of the method can be brought up to 1%.

SUMMARY

Using bismuth and lead as examples, the isotope dilution technique and procedure are described. The influence of a number of factors on the accuracy of the method has been studied; such factors include: the yield of the element to be determined, the concentration of the element in the sample to be analyzed, the ratio of the amount of the element to be determined to that of the indicator, the ratio of the specific activity of the indicator to that of the isolated compound. RaE (Bi^{210}) and ThB (Pb^{212}) isolated in a radiochemically pure state were used as radioactive isotopes. Bismuth was isolated as the phosphate and pyrogallate. In addition, bismuth and lead were determined by precipitation with ammonium benzenesulfinate.

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COPRECIPITATION OF ZINC, CADMIUM, AND MERCURY WITH ANTHRANILIC ACID

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Isolation of small amounts of materials by coprecipitation with organic carriers is a promising method of concentration. All the same, work on concentration and isolation of traces by this method is not numerous. Explanations of the principles and rules lying at the basis of the coprecipitation of micro amounts of materials with organic carriers are only just forthcoming at the moment [1-3]. The advantages of organic carriers have been examined in certain work [1, 4]. Excess of an organic precipitant which is sparingly soluble in a given medium has been recommended as an organic carrier for certain cations [5, 6].

The aim of the work described in the present article was a study of the coprecipitation of zinc, cadmium, and mercury with anthranilic acid precipitated from acid solutions. According to published results [7, 8], 0.35 g of anthranilic acid dissolves in 100 g water at 14°; this corresponds to 2.55×10^{-2} mole/liter; in addition the dissocation constant of this acid is known [8]:

$$\frac{[H^+]\,[C_6H_4(NH_2)\,COO^-]}{[C_6H_4(NH_2)\,COOH]} = 1.07 \cdot 10^{-5}.$$

On substituting $[C_6H_4(NH_2)COOH]$ in this equation by the value for its concentrated solution, we get:

$$[H^+]\,[C_6H_4(NH_2)COO^-] = 1.07 \cdot 10^{-5} \cdot 2.55 \cdot 10^{-2} = 2.7 \cdot 10^{-7}.$$

At high values of the hydrogen ion concentration (i.e. at low pH values) only a very small number of $C_6H_4(NH_2)COO^-$ ions remain in solution, and excess anthranilic acid is precipitated.

Using the method of radioactive indicators, we established that the precipitate of anthranilic acid which separated out in the presence of traces of certain cations, always contains the latter. The greater the amount of anthranilic acid precipitate, the greater the amount of various cations trapped. We do not have in mind in this connection the precipitation of the corresponding metal anthranilate, since the latter is only precipitated at comparatively high pH values.

We thought that coprecipitation with anthranilic acid is of practical interest, and, under certain conditions could be used for concentration of small amounts of certain elements. We studied the coprecipitation of zinc, cadmium, and mercury with anthranilic acid under various conditions.

Investigations were carried out by a micro method, involving the use of the radioactive isotopes Zn^{65}, Cd^{115}, and Hg^{203}. We were primarily interested in how the coprecipitation of one element or the other depends on the amount of anthranilic acid introduced into the test at various pH's. Experiments were carried out at room temperature.

0.2 ml of a solution of the metal salt containing 25 γ Me^{2+} (marked with its particular radioactive isotope) was introduced into a test tube, 1 ml of a buffer solution,* and various amounts of sodium anthranilate were then added.** The final volume was always 2.2 ml.

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* We used acetate buffer mixtures prepared according to Britton [9].

** We used a 10% solution of anthranilic acid prepared according to a published method [10, 11]; 0.1 ml of this solution contained 10 mg of $C_6H_4(NH_2)COOH$.

In order to obtain reproducible results several experiments were carried out, so that each point on the curves shown on the diagrams is the mean of three experiments carried out in parallel.

On adding a certain excess of sodium anthranilate, anthranilic acid started to separate out. Separation of this precipitate is a time reaction and is complete after 0.5-1 hour (Fig. 1). As one would expect, a greater amount of anthranilic acid was precipitated the lower the pH, and equilibrium was established more rapidly.

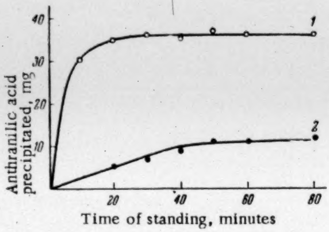

Fig. 1. Precipitation of anthranilic acid with time of standing:
1) 60 mg of anthranilic acid was introduced at a pH of 0.65; 2) 60 mg of anthranilic acid was introduced at a pH of 3.09.

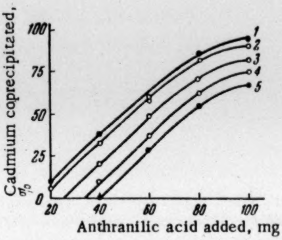

Fig. 2. Coprecipitation of cadmium as a function of the amount of anthranilic acid introduced (as sodium anthranilate):
1) pH 0.65; 2) pH 1.09; 3) pH 1.42; 4) pH 2.32; 5) pH 3.09.

Consequently, in all cases, the precipitate of anthranilic acid was centrifuged and removed from the mother liquor only after standing for one hour. The precipitate was dried at room temperature and weighed. The amount of Me^{2+} which had been coprecipitated was assessed on the basis of the activity of the mother liquor after removal of the anthranilic acid from it. The effect of the pH of the medium, and of the amount of sodium anthranilate on the coprecipitation of Me^{2+} with anthranilic acid was studied, taking cadmium as an example (Fig. 2) under conditions where cadmium itself is not precipitated when a definite excess of anthranilic acid is used.

The results obtained (Fig. 2) show that the greater the amount of anthranilic acid introduced, the greater the amount of it in the precipitate at a certain pH, and the greater the amount of cadmium coprecipitated with such a precipitate.

For the same amount of anthranilic acid, coprecipitation of cadmium is greater, the higher the acidity. Thus, on introducing 100 mg of anthranilic acid at a pH of 0.65, cadmium (25 γ) can be almost completely removed from solution (Fig. 2), while at a pH of 3.09, only 65-70% of the cadmium is removed. Consequently, it is also evident from Fig. 2, that coprecipitation of cadmium depends on the pH of the medium. While at a pH of 3.09 coprecipitation of cadmium starts on introducing more than 40 mg of anthranilic acid into the test sample, at pH 0.65 using the same amount of anthranilic acid, 40-50% of the cadmium is coprecipitated.

Figure 3 gives a clearer picture of the relationship between coprecipitation of cadmium and pH. It is clear from Fig. 3, that there is a linear relationship between the amount of coprecipitated cadmium and the pH of the medium.

For the same amount of added reagent, coprecipitation of cadmium decreases with increasing pH. We studied the effect of the pH of the medium on the amount of zinc and mercury coprecipitated with anthranilic acid (Fig. 4). In these cases 100 mg of anthranilic acid was introduced into a series of test tubes as sodium anthranilate. Other conditions being equal, it was found that zinc is coprecipitated to a greater extent than cadmium with anthranilic acid, while cadmium is coprecipitated to a greater extent than mercury (Fig. 4). There was again a linear relationship between the amount of Me^{2+} coprecipitated and the pH of the medium during coprecipitation of zinc and mercury, as was found in the case of cadmium.

From solutions whose pH is less than 1, micro amounts of zinc and cadmium can be extracted practically completely with anthranilic acid. Mercury is not completely removed under the given conditions. All the same,

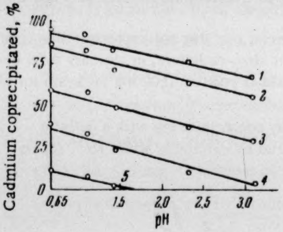

Fig. 3. Coprecipitation of cadmium with anthranilic acid as a function of pH. 1) 100 mg; 2) 80 mg; 3) 60 mg; 4) 40 mg; 5) 20 mg anthranilic acid.

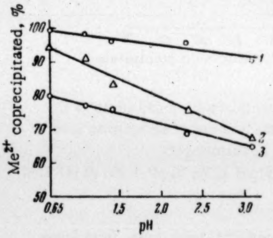

Fig. 4. Coprecipitation of zinc (1), cadmium (2), and mercury (3) with anthranilic acid as a function of the pH of the medium.

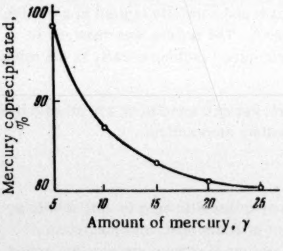

Fig. 5. Coprecipitation of mercury with anthranilic acid (100 mg) at a pH of 0.65 as a function of the amount of mercury in the test sample.

we observed that with decreasing amounts of mercury in the test sample, the completeness of its coprecipitation with anthranilic acid increases (Fig. 5). Experiments were carried out at a pH of 0.65; 100 mg of anthranilic acid was added to test samples followed by various amounts of mercury. We see that for the same amount of sodium anthranilate added, the percentage mercury coprecipitated is higher, the lower the content of mercury in the original solution. Thus, while 25 γ of Hg^{2+} at a pH of 0.65, and using 100 mg of anthranilic acid, is coprecipitated to the extent of 80%, 5 γ of mercury under the same conditions is extracted practically completely from solution by the precipitate of anthranilic acid.

We carried out experiments on coprecipitation of various amounts of zinc and cadmium with anthranilic acid, which also showed that coprecipitation of Me^{2+} depends on its initial amount in the test.

In all the experiments adduced above, the amount of coprecipitated Me^{2+} was determined in relation to the amount of anthranilic acid added as sodium anthranilate.

All the same, the amount of anthranilic acid introduced is not equivalent to the amount of it which is precipitated at a certain pH value (Fig. 6). Thus, on adding 100 mg of anthranilic acid to a test sample at pH 0.65, the amount of it which is precipitated is 45 mg, while at pH 3.09 only 20 mg of the anthranilic acid is precipitated. Consequently we thought it would be interesting to study coprecipitation of Me^{2+} in relation to the amount of anthranilic acid which is precipitated at a given pH value, and at a constant temperature. We studied this relationship taking coprecipitation of cadmium as an example. (Fig. 7). Experiments were carried out at 17° in solutions with varying pH. Curves 1-5 Fig. 7, show that coprecipitation of cadmium is greater, the greater the amount of anthranilic acid precipitated at a given pH.

For the same amount of precipitated anthranilic acid, the amount of cadmium coprecipitated is strongly dependent on the pH. For example, when there is 20 mg of precipitated anthranilic acid, the amount of coprecipitated cadmium can vary from 20 (pH 0.65) to 67% (pH 3.09). Consequently, pH changes affect coprecipitation in two ways. On the one hand, the lower the pH of the solution, the greater the amount of anthranilic acid precipitated (Fig. 6), and the greater the amount of the micro component coprecipitated. On the other hand, for the same amount of precipitated anthranilic acid, the amount of the micro component coprecipitated is higher, the higher the pH value (Fig. 7).

When using the phenomenon of coprecipitation for the purpose of extracting micro amounts of materials, of primary importance are the conditions under which this extraction becomes practically complete, and, in most cases, it is essential to know how much of the carrier is precipitated, since the micro amount must be freed from the latter. Accordingly, in a number of cases, it is more convenient to use the relation between the amount of the coprecipitated micro component and the amount of sodium anthranilate introduced (Figs. 2 and 3).

The experiments carried out enable one to choose the best conditions for carrying out coprecipitation (concentration) of Me^{2+} with anthranilic acid. For example, in order to extract zinc, cadmium, or mercury from their dilute solutions, it is necessary to add as large an amount of anthranilic acid as possible (100 mg for 2-2.5 ml of solution) to a solution with the lowest possible pH (pH 0.65).

The necessary degree of concentration of Me^{2+} is readily achieved by coprecipitating with a definite amount of precipitated anthranilic acid. Anthranilic acid is readily removed by calcining, while Me^{2+} (apart from mercury) is isolated as the pure oxide.

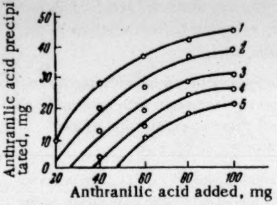

Fig. 6. Amount of anthranilic acid precipitated as a function of the amount of it introduced in the form of sodium anthranilate into the test at various pH's: 1) pH 0.65; 2) pH 1.09; 3) pH 1.42; 4) pH 2.32; 5) pH 3.09.

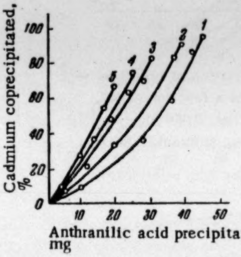

Fig. 7. Coprecipitation of cadmium as a function of the amount of anthranilic acid precipitated at various pH's: 1) pH 0.65; 2) pH 1.09; 3) pH 1.42; 4) pH 2.32; 5) pH 3.09.

Concentration and isolation of traces of Me^{2+} is possible when this method is used, even from large volumes of solution. Thus, 1.5×10^{-7} g·ion of zinc containing Zn^{65} as indicator (the specific activity was 210 impulses/minute per γ of Zn^{2+}) was separated by coprecipitating it with anthranilic acid from 100 ml of a solution with a pH of 0.65. Various amounts of anthranilic acid in the form of a 10% solution of sodium anthranilate were used for separating zinc. The anthranilic acid precipitated was allowed to stand for one hour, after which it was transferred to a filter. The filter was placed in a crucible and carefully ignited in a muffle. The precipitate in the crucible was then calcined for 20 minutes at 380-400°. The residue was dissolved in 0.5 ml of 1 N HCl and the amount of coprecipitated micro component determined radiometrically in the solution obtained.

The results obtained showed that 93-95% of 1.5×10^{-7} g·ion of zinc was extracted from 100 ml of a hydrochloric acid solution on adding 5-6 g of anthranilic acid in the form of sodium anthranilate.

SUMMARY

1. It has been shown that in the presence of the appropriate excess of anthranilic acid in acid solutions, the former is precipitated, starting at a pH of 3.09 and lower. The amount of anthranilic acid precipitated depends on the duration of precipitation, the pH of the medium, and the amount of sodium anthranilate added to the test.

2. It has been established that it is possible to coprecipitate zinc, cadmium, and mercury present in solution in micro amounts with anthranilic acid precipitated from acid solutions. All other conditions being equal, the amount of coprecipitated cation decreases in the sequence zinc, cadmium, mercury.

3. Conditions have been established whereby zinc, cadmium, and mercury can be extracted practically completely from acid solutions, by coprecipitation with anthranilic acid.

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AMPEROMETRIC TITRATION OF BISMUTH WITH POTASSIUM IODIDE IN THE PRESENCE OF PYRAMIDONE

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In a previous article [1] we showed that it is possible to carry out a direct amperometric titration of bismuth on the basis of the formation of the iodobismuthite of 8-hydroxyquinoline. On the basis of the capacity of bismuth ions to form a sparingly soluble complex with potassium iodide in the presence of pyramidone [2] – a complex which is similar to the iodobismuthite of 8-hydroxyquinoline – we decided to investigate the possibility of using this reaction for the quantitative determination of bismuth amperometrically.

For carrying out our experiments we used an ordinary visual polarographic setup with a dropping mercury electrode, and a saturated calomel reference electrode. The dropping time of the calomel electrode was 1 second. The bismuth sulfate was prepared by dissolving an aliquot of chemically pure metallic bismuth in sulfuric acid, to which had been added the nitric acid necessary to oxidize the bismuth. The amount of sulfuric acid taken was such that the acidity of the final solution was 2.5 mole/liter. Potassium iodide solution (0.35 M) was prepared from an aliquot of the pure salt.

A known volume of the bismuth salt was introduced into the beaker to be used for titration, pyramidone was then added, followed, when necessary, by other salts. The total volume and acidity of the solution being titrated was kept constant. After removal of dissolved oxygen by means of a stream of hydrogen, the solution was titrated with the solution of potassium iodide added from a micro buret. Titration was carried out under an applied potential of 0.5 volt.

As tests showed, the amount of bismuth found depends on the acidity of the solution being titrated. When the acidity was not high enough, the results obtained were too high. With increasing concentration of free acid the results become more accurate, and, at a content of 2.5 M, correct results are obtained. Nevertheless, on further increasing the acidity of the solution being titrated significantly, the results proved to be low, the error becoming more marked the higher the acidity.

This dependence of the results for bismuth determination on acid concentration, is, presumable, related to the effect of two factors operating in opposite directions; these factors are: hydrogen ion concentration and sulfate ion concentration. Usually, the solubility of the precipitate increases with increasing hydrogen ion concentration, as a result of which the rounding off on the titration curve increases. An increase in the concentration of sulfate ions in the solution being titrated should lead to a drop in the amount of potassium iodide used for titrating bismuth, since sulfate ions can form part of the complex instead of iodide ions. In all probability, at a sulfuric acid concentration of 2.5 M, the effects of the factors indicated above cancel each other out and correct results are obtained. Results of titration of the same amounts of bismuth, based on the anode current of the iodide ions, when both the factors indicated above act in the same direction, namely towards giving low results, confirm the explanation we have suggested for the effect of acidity during titration based on the cathode current of bismuth.

Increases in the amount of pyramidone by 2-4-10-20 and 40 times showed no effect, neither on the results, nor on titration of bismuth. Accordingly, in all experiments on titration of bismuth, the amount of pyramidone used was 500 mg/30 ml of solution.

The solutions being titrated, when they contained excess pyramidone, foamed strongly during agitation with a stream of gas, and this made titration difficult. We found that the addition of a small amount of alcohol, of the order of 8-10% by volume, almost completely destroyed the tendency of the solution to foam, and was found to have no effect on the results of titration. When too much alcohol was added, however, it was found that titration results were low.

TABLE 1

Results of Titrating Bismuth with Potassium Iodide (volume of solution being titrated 33 ml)

Bismuth taken, in mg	Bismuth found, in mg (average of 3-4 determinations)	Average reproducibility for bismuth, in %	Deviation of the mean amount of bismuth actually found from that taken	
			in mg	in %
38.65	38.32	0.18	—0.33	0.84
30.91	30.74	0.30	—0.17	0.55
23.12	23.13	0.71	+0.01	0.04
16.32	16.50	0.02	+0.18	1.13
10.28	10.64	0.76	+0.36	3.50
6.17	6.71	0.57	+0.54	8.71

As can be seen from the results given in Table 1, the titration results for different amounts of bismuth show a fairly good reproducibility, while experimental error does not exceed the permissible limits, when the amount of bismuth found is calculated on the basis of the theoretical titer of potassium iodide, on the assumption that the precipitate corresponds to the formula Pyr. $HBiI_4$.

During titration of solutions containing small amounts of bismuth, the results obtained were high.

As experiment showed, titration of bismuth is also possible without removal of dissolved oxygen, the accuracy being practically the same.

Results of titration of bismuth in the presence of various anions and cations are given in Table 2.

As the results given in this table show, nitrate ions do not interfere, even when their concentration is 60 times greater than that of the bismuth ions. At higher concentrations than this, nitrate ions depress the titration results; presumably this is related to the fact that at high concentrations, nitrate ions enter into the composition of the complex instead of iodide.

Chloride ions do not interfere at concentrations which are 50 times that of the bismuth. At higher concentrations, chloride ions also partially enter into the composition of the complex instead of iodide ions, thereby leading to low results for bismuth titration.

Acetic acid does not interfere with titration even when its concentration is 100 times that of bismuth. Phosphate ions do not interfere at a 45-fold concentration. Thus, bismuth can be titrated in the presence of considerable amounts of the anions of many acids. Iron, manganese, nickel, cobalt, zinc, chromium, aluminum, and magnesium ions do not interfere with bismuth titration even in those cases when the concentration of each of these ions is 50-100 times that of the bismuth ions. Cadmium, which accompanies bismuth in many alloys, does not interfere with bismuth titration, as long as the cadmium concentration is not more than 2.5 times the bismuth concentration. Higher concentrations of cadmium leads to high bismuth figures. Lead interferes, since it forms sparingly soluble lead iodide by reaction with potassium iodide. We tried to prevent interference on the part of lead by precipitating the lead beforehand as lead sulfate without filtration of the precipitate. Experiments showed, however, that such a technique only yields good results when the concentration of lead ions in the solution being titrated is equal to, or less than, the bismuth concentration. At higher lead concentrations, the results obtained for bismuth are low; this is presumable related to the fact that the lead sulfate formed traps some of the bismuth.

On the basis that some ions are capable of giving an anode current, and that iodide ions readily give such a current on a dropping electrode, we also decided to investigate the possibility of titrating bismuth with potassium iodide by the anode method. Titration was carried out under the same conditions as titration based on the cathode current of bismuth ions; the only exception was the voltage, which was 0.08 volt in these anode titrations. At this voltage, a diffusion current for iodide ions is obtained, while bismuth ions do not give a current. The titration curves obtained were of the ascending type. Titration had to be carried out in the presence of gelatine.

TABLE 2

Results of Titrating Bismuth in the Presence of Certain Ions (mean of 3-4 determinations)

Bismuth taken	Indifferent salt, R	$\frac{[R]}{[Bi]}$	Bismuth found, in mg	Deviation of the mean amount of bismuth actually found from that taken	
				in mg	in %
24.05	KNO_3	60	23.85	—0.20	0.83
24.05	KNO_3	100	23.14	—0.91	3.78
24.05	KCl	50	23.92	—0.13	0.54
24.05	CH_3COONa	40	24.01	—0.04	0.16
24.06	Na_2HPO_4	45	24.00	—0.05	0.21
24.05	CH_3COONa	100	24.00	—0.05	0.21
32.15	$(NH_4)_2\,SO_4$	100	32.12	—0.03	0.09
32.05	$CdSO_4$	2.5	32.31	+0.16	0.49
32.15	$CdSO_4$	5	33.02	+0.87	2.70
32.15	$FeSO_4$	50	32.00	—0.15	0.47
32.15	$MnSO_4$	50	31.98	—0.17	0.53
32.15	$MgSO_4$	50	32.03	—0.12	0.37
32.15	$NiSO_4$	100	32.01	—0.14	0.44
32.15	$ZnSO_4$	100	32.01	—0.13	0.14
32.15	$CoSO_4$	50	31.96	—0.19	0.59
32.15	$Cr_2(SO_4)_3$	50	31.97	—0.18	0.56
32.15	$KAl\,(SO_4)_2$	50	32.03	—0.12	0.37
32.15	$Pb\,(NO_3)_2$	0.5	31.94	—0.21	0.65
32.15	$Pb\,(NO_3)_2$	1	31.89	—0.26	0.81
32.15	$Pb\,(NO_3)_2$	2	30.71	—1.44	4.48
32.15	$Pb\,(NO_3)_2$	5	30.40	—1.75	5.44
32.15	$Pb\,(NO_3)_2$	10	29.12	—3.03	9.43

TABLE 3

Results of Titrating Bismuth by the Anode Method (mean results from 3-5 determinations)

Bismuth taken, in mg	Bismuth found, in mg	Mean reproducibility, in %	Deviation of the mean amount of bismuth actually found from that taken	
			in mg	in %
32.66	31.38	1.0	−1.28	3.91
16.44	16.23	1.2	−0.21	1.31
8.14	8.98	0.88	+0.84	10.13

TABLE 4

Results of Titrating Bismuth and Cadmium in a Synthetic Mixture (mean of four determinations)

Amount of bismuth that should be present, in %	Bismuth found, in %	Deviation of the amount of bismuth actually found from the true value, in %	Amount of cadmium that should be present, in %	Cadmium found, in %	Deviation of the amount of cadmium actually found from the true value, in %
45.29	45.49	0.44	54.71	54.19	0.95

As the results given in Table 3 show, titration of bismuth by the anode method gives considerably less accurate results than those obtained by using the cathode current of bismuth.

In order to check on the practical applicability of the method we have developed for determining bismuth, we carried out an analysis of a synthetic mixture of bismuth and cadmium. An aliquot of the mixture was dissolved in a mixture of nitric and sulfuric acids. The solution was transferred to a standard flask and made up to the mark with water. An aliquot part of the solution was taken for titration. Bismuth was titrated in one aliquot of the solution with a sulfuric acid concentration of about 2.5 M. Cadmium was not titrated under these conditions. In another aliquot, after precipitation of bismuth with ammonia according to the procedure outline in our article [3], cadmium was titrated at a voltage of 1 volt. The results obtained are given in Table 4.

As the results given in Table 4 show, the method we have suggested for determining bismuth gives satisfactory results.

SUMMARY

1. It has been shown that it is possible to titrate bismuth amperometrically with potassium iodide in a strongly acid solution, in the presence of excess pyramidone; the method is based on the formation of the tetraiodobismuthate of pyramidone, a dropping mercury electrode is used.

2. It has been established that zinc, manganese, nickel, cobalt, iron, aluminum, and magnesium do not interfere with the bismuth titration. Even considerable amounts of sulfate, nitrate, chloride, phosphate, and acetate ions do not interfere. Amperometric titration of bismuth has been checked on a synthetic mixture of bismuth and cadmium.

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DETERMINATION OF STRONTIUM IN ORES BY FLAME SPECTROPHOTOMETRY

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As a result of the similarity in the properties of strontium and calcium, there are no simple methods for the determination of the former which are suitable for studying ores. Normally, separation of the nitrates by treatment with a mixture of alcohol and ether is used [1]. The method is tedious and its accuracy is low, particularly at low strontium concentrations; before such a method can be used, it must be preceded by a long chemical preparation which consists in separating these metals from other metals, and preparing the mixture of nitrates.

Flame photometry has recently found application for the determination of strontium and other alkali-earth metals; using this technique, rapid methods for determining this element in water [2, 3], cement [4], oxide cathodes [5, 6], etc. [7, 8] have been developed. We thought it should be possible to use this method also for analyzing ores and minerals.

Apparatus

The flame spectrophotometer used was based on the UM-2 monochromator [9, 10]. A setup was prepared for the monochromator containing a FEU-19 photomultiplier, the output of which was connected to a sensitive mirror galvanometer [11]. A burner for producing an acetylene-air flame was fixed in front of the inlet slit of the apparatus, the burner being connected to a sprayer and an acetylene source. The apparatus is shown on Fig. 1.

Fig. 1. General appearance of the flame spectrophotometer based on the UM-2 monochromator.

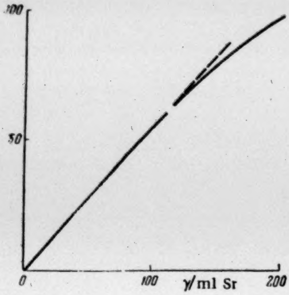

Fig. 2. Relation between intensity of the strontium radiation at 460.7 mμ and its concentration in solution.

The suitability of the apparatus for the problem in question was tested by determining the sensitivity and specificity for the determination of strontium. For a sufficiently high voltage on the photomultiplier (1800 volts) a sensitivity of 0.1-0.07 γ/ml (divisions) was achieved for strontium, i.e., the galvanometer needle moved through one division at a concentration of strontium in solution of 0.07-0.1 γ/ml. The resonance line 460.7 mμ for strontium was used. The width of the input and output slits of the monochromator was 0.1 mm. The radiation of the flame itself at this wave length is equivalent to about 6 γ/ml of strontium.

In order to establish the specificity of strontium determination, the values of the readings obtained for solutions of salts of strontium and other metals on the apparatus were determined, the strontium line 460.7 mμ being used. It was found that under these conditions, the concentrations of other metals had to be many times greater than that of strontium in order to give the same reading as the strontium solution. The numerical values of these concentration ratios – "specificity factors" – were found to be 11,000 for calcium and barium, 8,500 for sodium and 2,600 for potassium. Thus the apparatus assembled proved to be completely suitable for strontium determination. Determination of strontium on the basis of the molecular band at 670 mμ is considerably less specific.

Emission Characteristics of Strontium

The relation between the intensity of the strontium radiation and its concentration in solution is linear for concentrations up to 100 γ/ml (Fig. 2).

The intensity of the strontium radiation depends on the presence of a number of other materials in solution. Acids–nitric, hydrochloric, sulfuric and other acids – depress the brightness of the strontium illumination of the flame to various degrees; acetic acid on the other hand increases the brightness (Fig. 3).

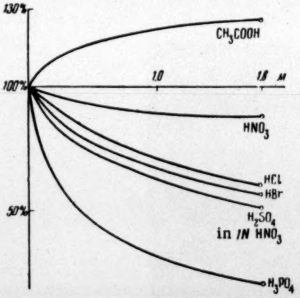

Fig. 3. Relation between the intensity of strontium radiation (100 γ/ml) and the concentration of added acids–acetic, nitric, hydrochloric, hydrogen bromide, and sulfuric (the latter was taken in the presence of 1 N nitric acid.

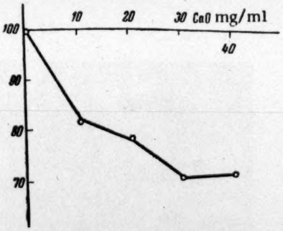

Fig. 4. Relation between the intensity of strontium radiation (50 γ/ml) and the concentration of added calcium nitrate in 0.5 N nitric acid.

Phosphoric acid in particular, as pointed out in the literature, exerts a particularly strong extinguishing effect [12, 13].

Of the metals, aluminum was found to exert an extinguishing effect on strontium illumination. As the results in Table 1 show – this table also contains results for calcium – a number of other metals also exhibit an extinguishing effect.

TABLE 1

Change in Intensity of Strontium Radiation at 460.7 mμ and of Calcium at 422.7 mμ (concentration of the solutions in terms of the metal −100 γ/ml) in the Presence of the Salts of Other Metals

Salt added	Concentration of metal added, in mg/ml	Radiation intensity, in %	
		Sr	Ca
Without any additives	—	100	100
Aluminum nitrate	1.5	10.7	15.0
Aluminum nitrate	3.5	0	2.2
Beryllium nitrate	2.0	40.5	52.5
Ammonium vanodate	2.2	20.0	35.6
Bismuth nitrate	5.0	88.0	85.0
Iron chloride	2.5	87.0	94.0
Thorium nitrate	10.0	59.0	52.5
Titanium chloride	1.0	32.7	18.0
Uranyl nitrate	2.0	60.0	59.0
Chromium nitrate	5.0 (Cr_2O_3)	96.5	68.0

The effect of calcium (25-100 γ CaO/ml) on the intensity of strontium radiation 50-100 γ SrO/ml) is, in general, insignificant – the intensity of the radiation increases in all by 3-4%, nevertheless, even this effect can be removed by addition of ammonium chloride to the solution until its concentration is 0.5 M. When a large excess of calcium is present, the intensity of the strontium radiation drops, however, this drop in intensity of the radiation ceases on reaching a concentration of 30 mg CaO/ml (Fig. 4).

Taking into account the relationships established, two variants were developed for determination of strontium in ores – one for use at low strontium concentrations, and one for use at high concentrations.

Determination of Strontium at High Strontium Concentrations (in carbonate-sulfate minerals)

The technique consists in breaking down the sample by fusion with sodium and potassium carbonates, dissolving the isolated carbonates of calcium and strontium in hydrochloric acid, and carrying out a flame photometric determination on the solution obtained after removal of the hydroxides of aluminum and other elements by precipitation with ammonia. 100 mg of ore is fused in a platinum crucible with 3 g of sodium and potassium carbonate, the melt is leached with hot water, and the carbonate precipitates filtered off and washed on the filter with 0.5% of sodium carbonate solution. The precipitate is washed off the filter (without unwrapping the latter) into a beaker with a small amount of water. The residue is dissolved in 25 ml of 5 N hydrochloric acid, part of the acid being used to treat the filter which is afterwards washed with water. The filtrate and washings are combined with the main solution. The combined solution is neutralized with concentrated ammonia solution until a yellow color appears when using 1-2 drops of Methyl Orange as indicator. 5 N hydrochloric acid is then added dropwise until a rose color appears; this solution is then carefully reneutralized with dilute ammonia 1 : 10 until the yellow color reappears. The solution is next heated to coagulate the hydroxides. On cooling, the solution is transferred to a 250-ml standard flask, and diluted to the mark with distilled water. The solution is filtered free of precipitate through a dry filter, and

TABLE 2

Standard solution, in ml		Content, in γ/ml	
Ca	Sr	Ca	Sr
–	–	0	0
0.25	1.25	5	25
0.5	2.5	10	50
1.0	5.0	20	100
1.5	7.5	30	150
2.0	10	40	200
2.5	12.5	50	250

TABLE 3

Composition of the mixture, in %				Ratio	Amount in solution, in γ/ml		Amount found in solution, in γ/ml		Experimental error, in %	
$SrCO_3$	$SrSO_4$	$CaCO_3$	$CaSO_4 \cdot 2H_2O$		Sr	Ca	Sr	Ca	Sr	Ca
80	—	20	—	6:1	95	16	97	15.4	+2.1	—4.0
78	—	—	22	5:1	83	17.3	82	17.2	—1.2	—0.6
50	—	25	25	1.5:1	59.5	31.6	61	33	+4.0	+2.3
—	81.5	—	18.5	9:1	81.5	8.6	81	9.4	—0.6	+9.3
—	33	—	67	1:1	31.6	31.2	34	31	+7.6	—0.6
—	90	—	10	19:1	172	9.2	176	10.2	+2.3	+10.9
—	94	—	6	30:1	180	5.6	183	5.0	+4.5	—10.8
—	11	—	89	1:4	21	83	20.5	80	—2.5	—3.6
—	2.5	—	97.5	1:1	4.8	91	5	88	+4.2	—3.3

the filtrate used for photometric determination, using the 460.7 mμ line and comparing the values with standard solutions. The standard solutions can be prepared so as to contain calcium; in such cases, after determining the strontium, calcium can be determined in the same solution flame photometrically, using the 422.7 mμ line for calcium; standard solutions are prepared by mixing standard solutions of calcium and strontium salts in the amounts indicated below, with 25 ml of a stock solution of ammonium chloride, and diluting the mixture to 50 ml with water.

The stock solution of 1 M ammonium chloride is prepared by exact neutralization of 50 ml of 5N hydrochloric acid with ammonia, and diluting the solution to 250 ml. Stock solutions of calcium and strontium chlorides are prepared by dissolving 250 mg of calcium carbonate and 168 mg of strontium carbonate separately in 10 ml of 5 N hydrochloric acid; the solution is accurately neutralized with ammonia (taking care not to use excess) using Methyl Orange as indicator, the solution is finally diluted (with water to the mark) in a 100 ml standard flask.

During the determinations, readings are taken for the test solution and for two standard solutions, one of which gives a higher reading, and the other a lower reading than the test solution. Measurements are also carried out in reverse, and the mean value taken. Calculations are made by graphical interpolation; the content of Ca (or Sr) found in γ/ml is divided by four to give the percentage content of the element in the test material.

A check test on mixtures of calcium and strontium carbonates and sulfates showed (Table 3) that it is possible, by using this method, to determine these elements with an average accuracy of 3-5% (relative).

Determination of Small Amounts of Strontium

By means of the method developed, it is possible to determine strontium conveniently for contents of this element as low as fractions of a percent. For determining even smaller amounts of strontium (down to a thousandth of a percent) it is necessary to take a large weight and to work with more concentrated solutions. The effect of calcium, which may be present in variable amounts, can be removed by carrying out flame photometric determinations in the presence of excess calcium, added in concentrations of 30 mg/ml. 1 g of sample is fused in a platinum crucible with 6 g of a mixture of sodium and potassium carbonates. The precipitate of the carbonates is filtered through a dense, ashless filter and washed with 0.5% sodium carbonate, and twice with distilled water. The precipitate is washed off the filter with a stream of water into a beaker and dissolved in 25 ml of 5 N nitric acid. The solution is heated almost to the boiling point, and iron, aluminum, manganese, etc. precipitated by dropwise addition of ammonia free from carbon dioxide until coagulation of the precipitate is complete. The precipitate is filtered off, washed with 2% ammonium nitrate and then discarded (if there is a large amount of precipitate it may be necessary to reprecipitate with ammonia). The solution is evaporated to approximately 40 ml and then transferred to a 50 ml standard flask, in which it is made up to the mark with water. Before carrying out flame photometric measurements, the solution is mixed with an equal volume of 1 N nitric acid containing 60 mg/ml of CaO as the nitrate.

TABLE 4

SrO found in solutions of ore samples, γ/ml	Mean	Added	SrO found in solutions to which SrO has been added, γ/ml	Added SrO found γ/ml
	SrO γ/ml			
5.9	5.85	10	15.8	10.0
5.8		10	15.4	9.6
40	40	50	89	49.0
40		50	91	51.0
21	21	25	45	24.0
21		25	46	25.0
6.9	7.0	10	17	10.0
7.2		10	17	10.0

During flame photometric determinations, readings for test solutions are compared with the readings obtained for standard solutions containing 1, 2, 5, 10, 20, 50, and 100 γ SrO/ml. A stock solution is first prepared containing 1 mg SrO/ml; this is done by dissolving 0.6408 g of $SrCl_2 \cdot 6H_2O$ in a 20% solution of ammonium nitrate; from this stock solution, by dilution with the same 20% solution of ammonium nitrate, standard solutions containing 2, 4, 10, 20, 40, 100, and 200 γ SrO/ml are prepared. These standard solutions were diluted to twice their original volume with a solution containing 60 mg CaO/ml in 1 N nitric acid (107 g of $CaCO_3$ is dissolved in 5 N nitric acid, 200 ml of the latter is added in excess and the volume made up to 1 liter).

Calculations are made according to the method outlined above. A content of 1 γ SrO/ml in solution corresponds to 0.01% of strontium in the test.

The method developed was checked by the method of additions (Table 4).

SUMMARY

Two variants of a method have been developed for the flame spectrophotometric determination of strontium in ores: 1) for large amounts of strontium and 2) for small amounts of strontium (0.1-0.001%). The flame spectrophotometer used was based on the UM-2 monochromator, a photomultiplier, and a galvanometer. Determinations were carried out on the basis of the 460.7 mμ line in an air-acetylene flame. The procedure involves decomposing the sample by fusing it with sodium and potassium carbonates in order to remove sulfates, and removal of interfering elements – aluminum and others – by precipitation with ammonia. The effect of variable amounts of calcium can be eliminated during determination of large amounts of strontium by flame spectrophotometry, by addition of ammonium chloride, while during determination of small amounts of strontium, the effect of variable amounts of calcium is eliminated by addition of calcium to both the test solution and standard solutions in amounts of 30 mg CaO/ml.

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QUANTITATIVE SPECTROGRAPHIC DETERMINATION OF GALLIUM IN SILICATE ROCKS AND MINERALS

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Gallium has been spectrographically determined by many research workers [1-8]. Goldschmidt and Peters [1] have determined gallium in a D.C. arc using carbon electrodes. Carbon powder plus sodium chloride have been used for stabilizing the burning of the arc. A mixture of aluminum oxide and quartz was used as a basis for preparing standards. S. A. Borovik [8] has used platinum as an internal standard. The composition of the base was as follows: SiO_2 30%; Al_2O_3 40%; $CaSO_4$ 20%; NaCl 10%, which only approximately corresponds to the average composition of rocks. It seemed to us that this technique could not be very accurate in view of the lack of agreement between the bulk composition of the rocks and the composition of the standards. Furthermore, it is very difficult to find aluminum oxide which is free from traces of gallium. Rusanov's method [9, 10] for determination of gallium in sulfide rocks and minerals is also not very suitable for gallium determination in silicates. In developing a technique for determining gallium in silicates, we followed the idea of using a "buffer," i.e., a material which is added in equal amounts to both the test samples and to the standards, and which determines the conditions of burning of the arc and its temperature parameters. When a buffer is used there is no need to prepare several series of standards for each type of rock. This method can be used for analyzing rocks and silicate minerals of any composition. In choosing a material for dilution we made use of the volatility series of Rusanov [11]. With respect to volatility, gallium is similar to copper, manganese, germanium, and iron. Manganese and iron cannot be used because their lines are located in the same region of the spectrum as the analytical lines of gallium, and mask the latter. Experiments with CuQ as a "buffer" did not yield positive results. Addition of CuO to the standards did not increase the sensitivity of gallium determination, and the burning of the arc was not very stable. Of the many "buffers" we tried, the most suitable ones proved to be alkali metal salts; particularly suitable were sodium chloride and lead sulfate. We finally settled for sodium chloride which satisfies all the requirements of a "buffer." Sodium vapor lowers the arc temperature and decreases the effect of other elements on arc burning; under such conditions the background decreases as well as the intensity of the iron line Fe 2943.57, so that it is possible to increase the sensitivity of gallium determination to 1×10^{-4}%, i.e., increase it ten times; arc burning is stabilized so that reproducibility of the results improves (Fig. 1).

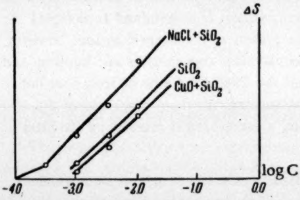

Fig. 1. Calibration curves as a function of the composition of the base used for preparing the standards.

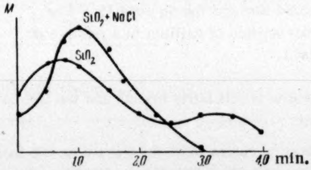

Fig. 2. Evaporation curves for gallium from pure SiO_2 and from a mixture of SiO_2 and NaCl.

Presumably, sodium chloride, being more volatile than gallium oxide, draws the gallium with it during evaporation (Fig. 2). Gallium evaporates completely in 2.5-3 minutes from a standard to which a "buffer" has been added (weight of standard 20 mg, weight of "buffer" 20 mg), while a silicate melt free from gallium holds back the gallium, and evaporation of the latter ceases after 4 minutes burning of the arc for a sample of 20 mg (current 10 amperes). This also explains the increase in sensitivity of the determination.

Synthetic standards were prepared from pure silica which had been checked for its purity beforehand spectroscopically. Gallium was added to the standard as Ga_2O_3. Standards were prepared with gallium contents ranging from 1 to 0.0001%. 0.005% of tin as $SnCl_2$ was added to the sodium chloride. The tin served as an internal standard.

Standards thus prepared, and test samples, were diluted with "buffer" in the proportion 1:2. The weight of standards and test samples after dilution with sodium chloride was 45 mg.

Gallium was determined on a ISP-22 spectrograph with a quartz optic of average dispersion; the slit width was 0.005 mm. Spectrographically pure carbon rods 40 mm long and 6 mm diameter were used as electrodes. Test sample was placed in a crater in the lower electrode, the crater being 3 mm in diameter and 6 mm deep. The upper electrode was sharpened to a cone. The excitation source was a D.C. arc operating at a voltage of 220 volts and 15 amperes; excitation occurred in the cathode layer; exposure time was 3 minutes.

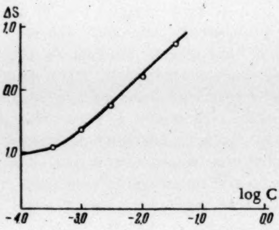

Fig. 3. Relation between relative blackening of the Ga 2943.64 line and the Sn 3034.12 A line, and the concentration of gallium in a mixture of SiO_2 and NaCl.

The plates used were "spectrographic plates for scientific use," type P, contrast, the sensitivity being 22 GOST units. The developer was metol-hydroquinone; development was carried out for 5 minutes at 18°. Photometric measurements were carried out on a MF-2 microphotometer.

We used the most sensitive line of gallium in the ultraviolet – the 2943.64 A line. The reference line was the tin line at 3034.1 A, whose excitation potential is near to that of the analytical line of gallium. The gallium line 2943.64 and the tin line 3034.1 A are homologous. The only drawback of the 2943.64 A line of gallium is that it is superimposed by a weak iron line at 2943.57 A, which leads to errors when gallium is determined in samples rich in rion. In the presence of sodium chloride, however, iron starts to evaporate after two minutes arc burning, and, more often than not the 2943.57 A line of iron does not appear at all in the spectra. In those cases where the spectrum of iron is still fairly intense and the 2943.57 A iron line appears, a correction is introduced (in ultrabasic rocks).

Calibration curves were constructed on the basis of the three standards methods. Standards with gallium concentrations of 0.01, 0.003, 0.001, 0.0003, and 0.0001% were photographed on one plate (three aliquots of each) as well as test samples (two aliquots each). Calibration curves were then drawn within the coordinates $\Delta S = f(\text{logarithm } C_{Ga})$,

where
$$\Delta S = \log \frac{S_{Ga}}{S_{Sn}} .$$

The relation between ΔS and logarithm C is only linear for concentrations greater than 0.001% Ga; at concentrations lower than this value there is a tendency for the curve to approach the abscissa asymptotically, as a result of the effect of the background, and, sometimes as a result of the iron line 2943.57 A.

For the determination of small gallium concentrations (from 0.001 to 0.0001% – ultra-basic rocks) it was necessary to resort to graphs where the logarithm of the relative intensity, logarithm I_{Ga}/I_{Sn}, was plotted on the ordinate, and not the relative blackening of the lines. The characteristic curve of the photographic plate for transition from blackening to intensity was constructed with the aid of a nine-stage reducer (Fig. 4). In order to

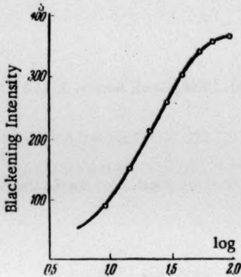

Fig. 4. Characteristic curve of the photographic plate.

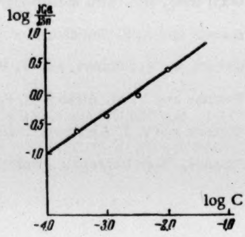

Fig. 5. Relation between the relative intensity of the line Ga 2943.64 A and the line Sn 3034.12 A, and the concentration of gallium in a mixture of SiO_2 and NaCl.

avoid curvature of the calibration curves as a result of superposition of the background, a correction was applied for the background in terms of the intensities of the gallium and tin lines. Values of $I'_{Ga} = I_{Ga} - I_1^{\cdot}$, and $I'_{Sn} = I_{Sn} - I_2^{\cdot}$, where $I_1^{\cdot}$ and $I_2^{\cdot}$ are the background intensities near the lines being measured, were plotted along the ordinate. The values of $I_1^{\cdot}$ and $I_2^{\cdot}$ were also found from the characteristic curve of the photographic plate. By switching from blackening to line intensity, and applying corrections for the background, it was possible to straighten out the calibration curves in the range of gallium concentrations less than 0.001% (Fig. 5).

TABLE 1

Gallium		
Introduced, in %	Determined, in %	Error, in %
0.0030	0.0032	6.6
0.0050	0.0054	8.0
0.0010	0.0009	10.0
	Mean	8.2%

The mean relative experimental error of the method is 8% (see Table 1).

The reproducibility error (arithmetic mean of 5 measurements) for concentrations greater than 0.001% gallium amounts to 3%; for concentrations less than 0.001%, it is 8%.

SUMMARY

A quantitative spectrographic method for determining gallium in various silicate rocks and minerals is described; it is based on the use of sodium chloride as a "buffer" with one series of standard mixtures. Sodium chloride, which is added to the sample in the proportion of 1 : 2, increases the sensitivity of gallium determination to 1×10^{-4}%, i.e., ten times. The mean relative experimental error is 8%.

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SPECTROGRAPHIC DETERMINATION OF CALCIUM, MAGNESIUM, COPPER, ALUMINUM, IRON, TITANIUM, AND BORON IN HIGHLY PURE SILICON

R. R. Shvangiradze and T. A. Mozgovaya

The presence of certain impurities, even in insignificant concentrations, leads to a considerable deterioration in the properties of semiconductors [1]. It is natural therefore, that in parallel with the question of preparing materials of a high degree of purity, there arises the problem of developing analytical methods with high sensitivity. Practice has shown that silicon which is to be used as a semiconductor should not contain certain impurities at levels higher than 10^{-5}-10^{-4}%. At such concentrations the methods of analytical chemistry are exceedingly cumbrous, and require the use of large amounts of pure reagents, the preparation of which in itself is a complex problem. Current spectrographic methods of analysis allow the determination of most elements in pure materials at concentrations down to 10^{-3}%. In order to increase the sensitivity, resort is often made to enrichment methods, or to complete removal of the required element [2-5]. This approach fundamentally complicates the technique of spectrographic analysis.

In the present article it is demonstrated that it is possible to determine low concentrations of certain impurities in highly pure silicon by a spectrographic technique, in which a careful choice has been made of excitation conditions, and the conditions used for registering the spectra.

Excitation Conditions

A D.C. arc ensures maximum sensitivity for the detection of elements in pure materials, although it does not give results with very good reproducibility. Using our technique, by means of a D.C. arc, the sensitivity of determination of many impurities in silicon, and also in germanium, could be increased by one order as compared with an activated A.C. arc of the Sventitsky type.

One of the main factors which limit the sensitivity of spectrographic analysis, is the background, which is caused by the continuous radiation from the spectrum excitation source, or by the rich spectrum of a main component with lines which are difficult to resolve. Even under the most favorable conditions, one cannot use for single determinations more than 100 mg of test material, since the increase in weight, and, consequently, the increase in exposure time, lead to such an intensification of the background that treatment of the spectrograms becomes impossible.

The silicon spectrum is poor in lines, but SiO_2 molecules which are formed in the arc, and which dissociate to only a small extent, give a multilinear band spectrum which gives an intense background, particularly in the short wave region of the spectrum registered on the ISP-22 spectrograph. In the long wave part of the spectrum, CN bands with even greater intensity appear. By altering the conditions used for exciting and registering the spectra, it is possible to achieve a relative decrease in background intensity, and to increase the sensitivity of detection of elements as a result of an increase in the difference $S_{L+B}-S_B$. On Fig. 1 are shown curves relating changes in the blackening density of certain analytical lines to the current; these were obtained during complete combustion of the test sample in anode craters 3 and 5 mm deep. The lines used for measurements are given on Fig. 1, the excitation energies of the respective lines being given in electron volts in brackets. Curves marked "a" are those obtained on using an anode crater 5 mm deep, while those marked "b" were obtained with a 3 mm deep anode crater. The curve marked "B" is the curve relating background blackening to the current at 2850 A. It is clear from Fig. 1 that the intensity of many spectral lines increases essentially on increasing the current. Changes in the current have only a weak effect on the intensity of magnesium lines and on those of the main component – silicon. At a current less than 6-7 amperes, the line intensity decreases, the burning of the arc is

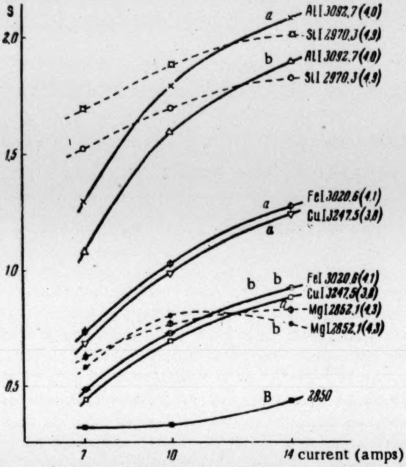

Fig. 1. Relation between line intensity and current:
a) When using an anode crater with a depth of 5 mm; b) using a crater 3 mm deep.

unstable, the time for complete burning of the sample increases, and the reproducibility deteriorates. Above 10 amperes the background complicates treatment of the spectrograms. For quantitative analysis of silicon therefore, an optimum current of 7-10 amperes was used. Increasing the depth of the anode crater (and the amount of sample accordingly) does not increase the intensity of the spectral lines appreciably.

Addition of graphite powder to the silicon leads to some increase in the ratio I_L/I_B, and to an essential improvement in the repeatability of the results. Two variants are described in this article for the analysis of silicon: one with addition of graphite powder, and the other without addition of graphite powder.

During burning of powdered test material in arc sources, there is observed a selective sequence in the passage of the components from the electrode crater to the gaseous discharge cloud.

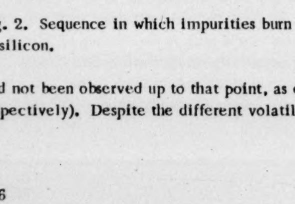

Fig. 2. Sequence in which impurities burn out of silicon.

The nature of the burning out of the impurities from metallic silicon and germanium, and from their oxides differ essentially from each other. From metallic powders the impurities pass into the gaseous arc cloud mainly in accordance with their volatility, as can be seen from Fig. 2, in the case of silicon, and from Fig. 3 for the case of germanium, on which are shown the general form of the relationship between blackening of the analytical spectral lines of the impurities and the burning time of the arc (impurity concentration 10^{-3}-10^{-4}%). In the case of the oxides of silicon or germanium, the major components (Si, Ge) are the first to evaporate preferentially. At the end of arc burning of the base, there is observed a sharp increase in the intensity of the lines of most of the impurities, or the first appearance of these lines which had not been observed up to that point, as can be seen from Figs. 4 and 5 (for silicon and germanium oxides respectively). Despite the different volatilities of the impurities, they basically burn out at the same moment

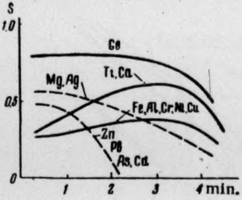

Fig. 3. Sequence of the burning out of impurities from germanium.

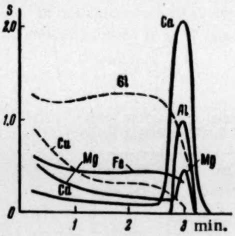

Fig. 4. Sequence of the burning out of impurities from silicon oxide.

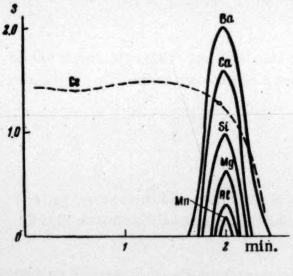

Fig. 5. Sequence of the burning out of impurities from germanium oxide.

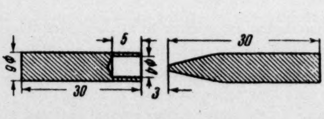

Fig. 6. Graphite electrodes.

of arc burning during the very short period of time when evaporation of the whole sample is practically complete. This "enrichment" phenomenon makes it possible to increase the sensitivity of qualitative detection of impurities considerably in pure materials, by photographing the spectra during the last stages of arc burning. The use of this phenomenon for quantitative analysis is complicated by the poor reproducibility both of the absolute and the relative intensities of the lines at this stage of arc burning.

Determination of Ca, Mg, Cu, Al, Fe, and Ti in Silicon. Standard samples to be used for constructing calibration curves were prepared by adding powdered metallic impurities to highly dispersed silicon powder. Initially a standard with a high concentration of the impurity was prepared, then, by dilution of this standard with spectrographically pure silicon, a series of standards were prepared with an impurity content ranging from 10^{-2} to 10^{-5}%. The uniformity of the distribution of impurity in the general mass of the standard, for the case of certain elements (Fe, Ca), was checked by the radioactivation method. It was found that by careful trituration of the test sample in an agate mortar for 1 hour, the nonuniformity of the distribution amounted to ± 3%. The correctness of the absolute concentrations of the impurities in certain standards was checked by chemical analysis. The standards used were similar silicon preparations analyzed in two different chemical laboratories.

Silicon was analyzed under the conditions described below. The electrodes were fired in the arc at a current of 14 amperes for one minute in order to remove surface contamination. The anode crater was filled with a mixture of silicon and carbon powder in the proportion of 4 : 1, and, with the slit of the ISP-22 spectrograph open, operated at a current of 10 amperes. By using the diaphragm of the intermediate lens of a three lens illuminating system, the radiation of the central part of the inter-electrode space was cut out. The height of the cut out of the diaphragm was 3.2 mm the length being 10 mm. The spectrograph slit width was 10 μ. Spectra were photographed during the course of the complete burning out of the test; the time taken was 180 ± 15 seconds. The moment of complete burning out was fixed by a drop in arc current of 0.6-0.8 amperes. Under these conditions, the molecular spectrum of CN was so intense that the analytical lines of calcium could not be seen. In order to determine Ca, the excitation conditions and the conditions used for photography in the second variant were chosen so that the CN bands were significantly weakened. Silicon was not mixed with carbon powder, while the current used was dropped to 7 amperes, and the height of the cut out of the diaphragm was decreased to 2.0 mm, and the crater depth reduced to 3 mm. Complete burning out of the sample in this case took 190 ±15 seconds. All the other conditions were left unchanged.

The spectra of standard samples were registered twice, whichever variant was used, on three photographic plates —

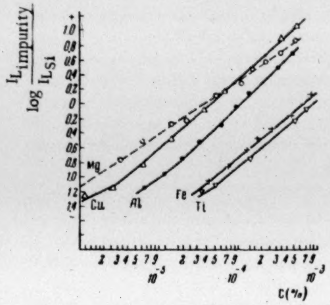

Fig. 7. Calibration curves for determination of Mg, Cu, Al, Fe, Ti, in Si (First variant).

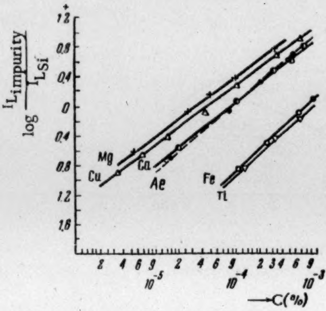

Fig. 8. Calibration curves for determination of Ca, Mg, Cu, Al, Fe, and Ti in Si (Second variant).

TABLE 1

Test element	Analytical pairs of lines	Concentration range determined from - to $x \cdot 10^{-4}$%		Mean arithmetic error of a single analysis, %	
		First variant	Second variant	First variant	Second variant
Ca	Ca 3933.7/CN 4026.5	—	1.0—100	—	32
Mg	Mg 2852.1/Si 3020.0	0.1—50	0.3— 50	9	14
Cu	Cu 3247.5/Si 3020.0	0.1—50	0.3— 50	11	15
Al	Al 3092.7/Si 3020.0	0.5—70	1.0—100	7	17
Fe	Fe 3020.6/Si 3020.0	3.0—300	10—500	7	13
Ti	Ti 3234.5/Si 3020.0	5.0—500	10—500	8	15

spectrographic, type II. Treatment of the photographic emulsions was the standard one. Using the mean values of the relative intensities of the chosen pairs of lines, calibration curves were constructed within the coordinates:

$$\text{logarithm} \frac{I_{L_{impurity}}}{I_{L_{Si}}} - \text{logarithm } C_{impurity}.$$

The analytical pairs of lines, the concentration range determined, and the mean arithmetic error for a single analysis are given in Table 1. The calibration curves obtained for the first variant are shown on Fig. 7, while those for the second variant are shown on Fig. 8.

The choice of the Si 3020.0 A line as a reference line for all the elements (with the exception of calcium) was called for by the poverty of the silicon spectrum in lines of the required intensity. No silicon lines suitable for comparison could be found near the analytical lines of calcium; this was the factor that determined the use of the molecular spectrum of CN as a reference line.

Determination of Boron. The bands of SiO molecules which arise during arc burning in air, are particularly intense in that region of the spectrum in which the analytical lines of boron are located. In order to avoid the molecular spectrum of SiO, determination of boron was carried out in a special quartz flask in a nitrogen stream. The flask (Fig. 9) has two ground glass joints sealed with two matching rubber stoppers 1, through the center of which pass metal rods used for holding the graphite electrodes. To the upper rubber stopper is fitted a metal ring 2 with four screws 3 for centering the electrodes. Into one side of the flask is fused a flat, transparent quartz window 4 for the radiation to come out, while through the other side there is fused a vacuum tube 6 through

TABLE 2

Sample number	Found spectrographically (× 10^{-4}%)					Found chemically (× 10^{-4}%)				
	Ca	Mg	Cu	Al	Fe	Ca	Mg	Cu	Al	Fe
1	26.0	2.3	0.6	5.2	<1.0	35.0	1.8	1.1	8.0	<1.0
2	31.0	0.98	1.3	2.2	15.0	20.0	1.0	1.0	1.0	11.0
3	2.3	3.8	<0.1	<1.0	<1.0	2.0	5.9	<0.1	—	<1.0
4	8.3	1.6	0.3	1.4	<1.0	6.0	2.6	1.0	—	<1.0
5	1.36	0.5	<0.1	2.7	9.0	<2.0	1.3	<0.1	5.0	15.0
6	1.7	0.92	0.7	<1.0	<1.0	3.0	1.0	1.0	<1.0	<1.0
7	8.0	0.57	0.57	<1.0	<1.0	5.0	0.4	1.0	<1.0	<1.0
8	1.2	0.26	0.3	0.65	11.0	2.5	1.0	0.25	<1.0	5.0
9	2.0	0.6	<0.1	<1.0	<1.0	2.5	0.8	<0.1	—	<1.0
10	1.3	0.1	<0.1	<1.0	<1.0	<2.0	<0.1	<0.1	—	<1.0

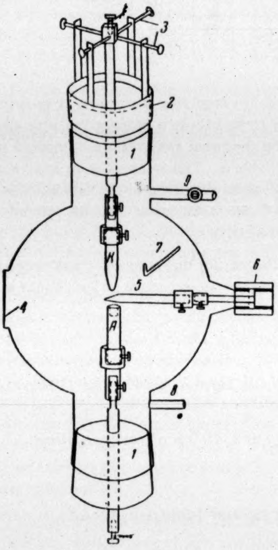

Fig. 9. Apparatus for determination of boron in a nitrogen stream.

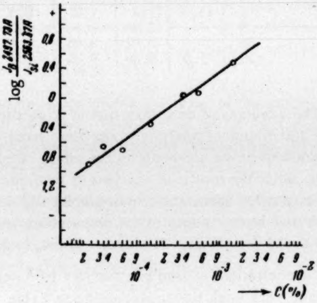

Fig. 10. Calibration curves for determination of boron in silicon.

which is packed the firing electrode 5; the latter, after igniting the arc, is pulled out from it and held by hook 7. The flask also has two other tubes 8 and 9 for pumping out the air and leading the stream of nitrogen into the flask respectively.

Boron was determined as follows. The electrodes (the anode has a crater 3 mm deep, and is 4 mm in diameter; the cathode is pointed) were given a preliminary firing in a D.C. arc for one minute in air. The anode crater was packed with powdered metallic silicon and the arc struck in a nitrogen stream at a current of 5 amperes (circuit potential 220 volts). In this case the ISP-22 spectrograph with one condenser for illuminating the slit was used. The spectrograph slit was 15 μ. The spectra were registered on photographic plates type P, in the course of 2.5 minutes, after a 5 second firing of the electrodes with the test sample. The calibration curves for the analytical pair of lines B 2497.73/Si 2563.67 A is shown on Fig. 10. The lowest detectable concentration of boron was 1.5-2.0 × 10^{-4}%. The probable error amounts to ± 15%.

Standards containing boron were prepared by diluting mixtures of Si and B with spectrographically pure silicon. The points obtained for these standards and for test samples of silicon, analyzed by a chemical method, lie on one calibration curve.

Reproducibility and Accuracy. As can be seen from Table 1, in addition to a certain increase in sensitivity, reproducibility also improves, when the first variant is used, as the result of stabilization of the burning of the arc on addition of carbon powder to the test, and increasing the current. The reason for the unsatisfactory reproducibility in the case of calcium determination is the use of the band spectrum of the CN molecule 4026.5 A as a reference line.

TABLE 3

Sample number	Added $(x \cdot 10^{-4}\%)$					Determined $(x \cdot 10^{-4}\%)$				
	Ca	Mg	Cu	Al	Fe	Ca	Mg	Cu	Al	Fe
1	3.4	4.5	3.3	5.8	—	3.7	4.2	2.5	4.7	—
2	5.3	7.9	6.7	9.2	4.0	5.2	10.0	5.0	8.8	4.3
3	7.5	14.5	13.3	15.8	13.3	9.5	12.5	12.5	9.3	12.0
4	2.5	2.1	0.7	8.8	24.0	2.8	3.0	0.6	7.6	27.0
5	7.0	6.2	12.7	55.0	6.7	7.5	5.9	14.0	62.3	8.6
6	1.1	5.1	5.0	5.0	50.0	1.3	5.2	5.0	3.0	41.4
7	14.0	11.2	1.3	6.3	13.5	12.5	12.4	0.9	7.0	16.0
8	—	0.36	1.4	3.7	—	—	0.4	1.5	3.9	—
9	62.0	0.67	0.85	4.4	11.0	53.0	0.74	0.88	4.2	11.0
10	1.5	0.25	0.25	1.8	5.0	1.2	0.30	0.29	1.6	5.6

The accuracy of determination of impurities in silicon was checked by comparing the results of spectrographic and chemical analysis on the one hand, and by determining the impurities in a preparation with known concentrations of the elements on the other. Results of spectrographic and chemical analyses are compared in Table 2, while the results of analyses of synthetic mixtures are given in Table 3. Test samples were analyzed chemically twice each, and spectrographically 3 times each. The mean values are given in the tables. The titanium and boron content of the preparations whose results are given in Table 2 was lower than the given method could determine. Titanium was not, in general, determined chemically.

Concentrations of iron less than 3×10^{-4} were evaluated by extrapolation; for this purpose it was necessary to measure very weak lines. According to Table 1, the results are reliable for concentrations of iron equal to $3 \times 10^{-4}\%$.

SUMMARY

A method has been developed for the quantitative determination of Ca, Mg, Cu, Al, Fe, and Ti in silicon of high purity.

A special method has been developed for the determination of down to $2 \cdot 10^{-4}\%$ of boron in silicon.

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SPECTROGRAPHIC DETERMINATION OF GOLD, PLATINUM, PALLADIUM, AND RHODIUM IN POOR PRODUCTS (ORES, SLAGS, AND WASTE SOLUTIONS)

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Spectrographic analysis is not sensitive enough for the direct determination of gold, platinum, palladium, and rhodium (0.0001-0.0002%) in ores, slags, and production solutions. In addition, the changing composition of test samples complicates direct spectrographic determination of these elements on account of the influence of third elements. Accordingly gold, platinum, palladium, and rhodium are preliminarily separated with copper. The sensitivity of determination of these elements in a copper bead is shown in Table 1.

For the spectrographic determination of these elements in samples containing 1-2 g/ton of the platinoids (total), it is necessary to carry out a preliminary enrichment of 30-50 times. Thus, if they are to be separated in a copper bead weighing 0.1-0.2 g, then the original sample weight will not be greater than 5-10 g. Such a weight of test materials is readily amenable to a chemical treatment which consists of the following.

5-10 g of test material which has been finely ground to pass through 150 mesh (the actual amount taken for a determination, which depends on the probable content of the noble metals in the test material, should be chosen so that it gives a content of 0.005-0.1% of the metals in the bead) is calcined in a muffle at 500-600° for removing any organic compounds or sulfur which may be present. The calcined test is transferred to a flask, moistened slightly with water, and 0.5-1.0 ml of formic acid added to reduce palladium, which may be present as its oxides. The test is heated to remove the formic acid completely and then 50-60 ml of aqua regia added. The flask + test material is then covered with a watch glass and the whole boiled for 1.5 hours. 55-60 ml of 1 : 1 sulfuric acid is added to the solution. The solution is twice evaporated in the course of 1-1.5 hours for complete removal of nitrogen oxides. The solution is finally cooled and 15-20 ml of hydrochloric acid and 0.3 g of potassium chloride added to it. The solution is gently warmed to remove most of the chlorine, after which it is diluted with hot water and filtered under vacuum. A solution of $CuSO_4$ is added to the filtrate in such amount that the copper content (the copper content of the material itself, which has been determined beforehand, plus the copper added as copper sulfate) amounts to 0.1-0.2 g; the solution is heated to the boiling point, and the copper together with gold, platinum, palladium, and rhodium precipitated with a 40% solution of sodium thiosulfate.

The precipitate of copper sulfide which has trapped the noble metals is filtered through an ashless filter, and carefully washed free of iron and thiosulfate with hot water, acidified with sulfuric acid, is finally dried, and then calcined in a muffle at 800-850°. The cupric oxide thus formed is reduced in a tubular oven in a stream of hydrogen at 400-500°. The reduced copper is placed in a graphite crucible and fused in an arc oven.

TABLE 1

Element	Sensitivity of the determination	
	in %	in g/ton
Gold	0.0003	3
Platinum	0.0010	10
Palladium	0.0030	30
Rhodium	0.0005	5

In those cases where the silicates of the metals it is required to determine may be present, for improving the decomposition after preliminary calcining of the test sample, an amount of ammonium fluoride equal in weight to the sample is added to it. When solutions are to be analyzed, the first stage of the operation – getting the test elements into solution – can be omitted; a solution of $CuSO_4$ and some sulfuric acid are added to the requisite amount of test solution; precipitation and subsequent treatment of the precipitate is then the same as described above.

The copper bead containing platinum, palladium, gold, and rhodium is then analyzed spectrographically.

The bead is introduced into an activated A.C. arc struck between electrodes of spectrographically pure carbon. A crater 3 mm in diameter and 1 mm deep is bored in the lower electrode. The upper electrode is ground to a flat surface. The inter-electrode distance is 2-2.5 mm, current strength 4.0 amperes, the voltage 220 volts. The slit width of the ISP-22 spectrograph is 0.010 mm; illumination is provided by a one lens quartz spherical condenser with f = 75 mm. The distance of the condenser from the slit is 315 mm and from the arc 100 mm. The plates used are spectrographic, type P, 9 x 12. Preliminary ignition is 30 seconds. The spectrum of each bead of test and standard is photographed twice with exposure times of 30 and 60 seconds.

TABLE 2

Analytical lines	Reference lines
Au 2675.95	Cu 2445.0
Pt 2659.45	
Pd 2447.91	
Rh 3434.89	Cu 3375.67

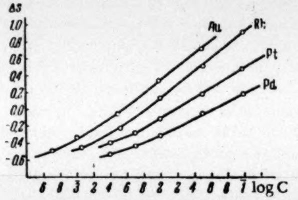
Development is carried out in a standard metol-hydroquinone developer. Determination can be carried out by either the three standards method or by means of a three dimensional graph.

Spectrograms are measured photometrically on an MF-2 microphotometer. The analytical pairs of lines used are given in Table 2.

Calibration curves are shown on the diagram.

Having determined the contents of the test elements in the copper bead, and knowing the weight of the copper bead and the original weight of sample taken (or the amount of solution taken), it is easy to calculate the amount of these elements in the test sample.

In order to check that all the noble metals have dissolved in the solution obtained after filtration, the insoluble residue is subjected to complete decomposition with hydrofluoric acid and then the noble metals dissolved in aqua regia. Since most doubt attaches to complete solution of platinum and palladium, treatment with hydrofluoric acid is carried out in a gold vessel. Tests have shown that the content of platinum and palladium in the insoluble residues does not exceed 5% of their total amount in the test sample, and, usually, it is considerably less. In the case of poor materials therefore the undissolved amount can be ignored.



Completeness of removal of the noble metals by means of sodium thiosulfate was checked both chemically and spectrographically. After isolation of known amounts of platinum and palladium, they were determined gravimetrically and photocolorimetrically.

For carrying out a spectrographic check, known amounts of gold, platinum, palladium, and rhodium are added to blank tests, and, after taking the material thus obtained through all the process of chemical enrichment, the bead finally obtained is analyzed spectrographically. Results of such experiments are given in Table 3. As these results show, the values obtained indicate approximately 100% extraction.

TABLE 3

Method used	Completeness of precipitation, in %			
	Platinum	Palladium	Gold	Rhodium
Gravimetric	97.2	–	–	–
Photocolorimetric	98.3	99.3	–	95.0
Spectrographic	101.8	97.1	102.0	96.3

Small weights of sample from 5-10 g provided the biggest difficulties for determination of noble metals in ore tests. Attempts to resolve the difficulties did not give positive results since all the formulas proposed for determining the amount of test material necessary are very approximate, and, since they have been derived by different authors, on the basis of different assumptions, the formulas often give contradictory results. There remains only a direct experimental-statistical method of solving this problem. The following system is adopted. Two parallel determinations are made on an ore sample by the copper bead method, using 5-10 g samples. At the same time, total platinum and palladium is determined on the same ore on samples of 100-300 g by an assay method. If the deviation between the results obtained is greater than the permissible value (accepted for the assay method), the analysis is repeated by both methods. On the basis of the analyses of several thousand samples, it was established that about 85% of the samples give satisfactory results during the first comparative tests. On repeating the analysis it was found that in approximately half of the remaining 15%, the error lay with the assay method. Thus, the error of the spectrochemical method developed amounts to 7-10% of the total number of analyses.

Some of the error is caused by insufficient care and accuracy in chemical treatment of test samples, while some of it is caused by a "fall" in the results particularly in the spectrographic part of the analysis. A large percentage of the deviation is arbitrarily explained by nonuniform distribution of the noble metals. In the course of our work we have come across some individual "stubborn" samples – not more than 1-2% of the total number of samples – which, even on repeated analyses gave very diverse results. In these samples the noble metals are, presumably, present in the form of large grains (consequently, it is necessary to carry out at least two parallel determinations).

TABLE 4

Element	Upper limit as % of copper	Lower limit as % of copper
Platinum	0.1	0.001
Palladium	0.1	0.003
Gold	0.1	0.0003
Rhodium	0.1	0.0005

The relative error of one determination does not exceed ± 12%. This method therefore competes successfully with chemical methods for poor materials. When the content of the noble metals is greater than 20 g/ton, the spectrographic method is inferior to the chemical method in accuracy.

Standards for the analysis are easily prepared by fusing appropriate amounts of platinum, palladium, gold, and rhodium with copper in graphite crucibles in an arc or kryptol furnace. In Table 4 are given the limiting contents of platinum, palladium, gold, and rhodium which are suitable for spectrographic determination in copper beads. The first (richest) standard is obtained by fusing the original melts with pure copper. The other standards are prepared by diluting the first standard with pure copper. Chemical control of the composition of the standards is desirable, but not essential, since the accuracy of chemical analysis is lower than the accuracy of preparing synthetic mixtures; chemical analysis will only detect large errors.

Standards are introduced into the arc in the form of lumps weighing 0.10-0.15 g; they immediately fuse in the arc to form beads.

V. Ya. Vankin,[*] V. L. Ginzburg, I. N. Gramenitsky and Yu. L. Polyakin also participated in developing the method described.

SUMMARY

A method has been developed for the determination of platinum, palladium, gold, and rhodium in poor materials, which is based on the quantitative precipitation of these metals with copper from acid solution by sodium thiosulfate. All the precious metals are concentrated in a copper bead obtained from the precipitate. The copper bead is then analyzed spectrographically in an A.C. arc. The method is highly sensitive and permits analysis of samples containing tenths of a gram in a ton of material, the initial sample weight being 10 g. The method has been checked during experimental work extending over several years on ores, slags, and other materials.

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[*] Deceased.

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RAPID LUMINESCENT DETERMINATION OF URANIUM IN SOLUTIONS

A. F. Fioletova

One method used for determining uranium, is to prepare a bead of pure nonluminescent NaF on the loop of a platinum wire 1.8-2 mm diameter; when the bead is cooled, it is dipped in the test solution and then heated in a burner until the bead is completely fused. On cooling, the intensity of the luminescence of the bead is compared with the intensities of the luminescence of beads on a visual scale, these beads having been prepared in the same way from solutions with known uranium contents, or the luminescence of the test bead is compared with the intensity of the luminescence of glass standards by means of a GOI FM-42 fluorimeter.

The main difficulties involved in using this technique are caused by other elements which may be present in the test solutions. We have studied the effect of a large number of elements of the Periodic System and have established that the strongest luminescence quenchers are V, Cr, Mn, Fe, Co, Ni, and also those elements which form colored or black oxides (Pu, Cu). In addition, a number of elements (Ca, Mg, Ba, and Cd) though not quenching the uranyl luminescence change the color of the luminescence.

The effect of all these other elements can readily be removed by the simple and effective technique of dilution and the use of artificial additions.

On diluting the test solutions, the effect of the other elements decreases ten times more rapidly than the fluorescent intensity of the uranyl. Experiment has shown that in the vast majority of cases, a ten-fold dilution of the test solutions is sufficient to practically destroy the effect of these other elements. When the content of other elements is high it is advisable to check the value obtained on ten-fold dilution; this can be done by carrying out determinations at other dilutions as well (20, 50, and 100-fold). If the results obtained, after appropriate calculation, are in agreement, this indicates that the values obtained are correct.

Dilution cannot be used when the uranium content is less than 1×10^{-7} g uranium/ml of solution, since the results obtained in such cases are beyond the limits of the visual scale of standards, and the limits of the fluorimeter standards. Consequently, when the uranium content is very low, while the content of the quenching element is very high, one has to resort to introducing synthetic additions. After determination of the uranium in the test solution by the usual immersion, a standard solution of uranium is added to the test solution, and the final solution thoroughly mixed, the amount of uranium added being such, that it brings the total amount of uranium in solution up to a level which is twice that of the uranium content as determined by immersion in the original solution. The uranium content is then determined again by immersion.

In the absence of a quenching element, or when the content of the latter was low we obtained twice the amount of uranium, while at high contents of the quencher, we obtained another value which was smaller as a consequence of partial quenching of the uranyl luminescence. Under such conditions, the degree of quenching of the uranium added will serve as a measure of the quenching of uranium contained in the test solution.* Thus if the amount of uranyl added to the original solution is 50% quenched, it means that the test solution itself contained 50% more than was originally determined; if percentage quenching is 25%, this means that the test solution contained 25% more than that found originally, etc. Thus corrections can be applied to the results obtained by the usual immersion method.

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* The degree of quenching of the fluorescence of U not only depends on the concentration of the quencher, but also on that of U itself. Nevertheless, at similar concentrations, the degree of quenching differs very little and can be regarded as constant within the limits of experimental error.

It is convenient to add the uranium in the form of one of the concentrated standard solutions (1×10^{-3} or 1×10^{-4} g/ml). This simplifies the work, since it is then possible to add very small volumes (by means of a micropipet or microburet) and such volumes need not be taken into account when making the final calculations of the uranium content.

The technique of artificial additions is theoretically applicable to any content of uranium and quencher, but, in practice it is best used only when it is impossible to use the dilution technique, since the former technique takes longer (15-20 minutes for one determination).

The dilution principle was first employed by Northup [1]; he diluted the melts,not the solutions. On obtaining quenched dark beads, he added to them new portions of NaF, and the uranium luminescence appeared. Uranium was only determined qualitatively. The same technique has been described in the book on the Analytical Chemistry of the Manhattan Project [2]. The method of additions is also described there. The Americans use it in a different way from us; they introduce the solutions to be added in the tablets for the fluorimeter during their preparation. The combination of the techniques of dilution and artificial additions permits one to avoid the normally complex chemical methods of preliminary separation of quencher from uranium.

The reproducibility of the immersion method, i.e., the mean relative error, when using the techniques of dilution and artificial additions, both during visual determination and during determination by means of a FM-42 fluorimeter, varies around ± 10%. The same reproducibility is given by chemical methods where uranium is separated beforehand.

SUMMARY

Improvements in the rapid luminescent method of determining uranium in the presence of other elements are suggested.

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DETERMINATION OF OXYGEN AND HYDROGEN IN TITANIUM

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It is known from published sources [1] that titanium vigorously absorbs hydrogen (up to 33 atom.%) thereby formina a solid solution. Within the limits 47.4-62.4 atom.% there is formed a hydride phase of penetration with a variable composition $TiH-TiH_2$. At temperatures above 800° the solubility is proportional to $\sqrt{p}$ and decreases with increasing temperature. Consequently, when titanium is heated under vacuum the hydrogen is released.

When titanium is heated it is also capable of absorbing oxygen (up to 30 atom. %); it can also absorb other gases, nitrogen for example, to smaller extents. Oxygen and nitrogen also form very infusible compounds, TiO, Ti_2O_3, TiO_2, and TiN with titanium. For example, the melting point of TiO_2 is approximately 1800°, while its boiling point is 3,000°; the melting point of the nitrides is 2950°.

Titanium dioxide is reduced by carbon, probably in three stages:

1. $2\,TiO_2 + C = Ti_2O_3 + CO$ at ~ 1200°
2. $Ti_2O_3 + C = 2\,TiO + CO$ at ~ 1400°
3. $TiO + 2C = TiC = Co$ at ~ 1600°.

Titanium nitrate is exceedingly stable. When one compares the temperatures at which the dissociation pressure of the nitrides of various elements is equal to 1×10^{-3} mm Hg, one finds that this temperature is 1491° in the case of niobium, 1460° for tantalum, and 2331° in the case of titanium.

The capacity of titanium to yield dissolved and chemically combined hydrogen on heating it under vacuum, and also the capacity of carbon, at a certain temperature, to reduce titanium oxides, have been used for developing a technique for determining oxygen and hydrogen in titanium.

Practically all the hydrogen is liberated on heating titanium under vacuum at a temperature of 1000°. Titanium oxides on heating in graphite crucibles at temperatures of 2000° are completely reduced.

For determining gases in titanium, vacuum fusion employing an iron bath [2-5], or coarse graphite powder was used. Coarse graphite powder suggested by Walters [6] ensures results with good repeatability. The most favorable conditions for reducing the oxides are obtained by sprinkling graphite powder (10-20 mesh) into a crucible to a third of its height. It was established in special tests that fine graphite power cannot be used for this purpose, since the fused titanium forms a carbide film on the surface of the powder, and does not penetrate inside the grains.

When graphite powder is used not only favorable reducing conditions are obtained, but, in addition, the possibility of absorption of liberated gases by the pulverized titanium is eliminated. Titanium is one of those elements which is readily volatile under vacuum, consequently, during fusion it evaporates intensely. Pulverized titanium is a very active "getter." When graphite powder is used, the titanium readily forms carbide; at the same time CO is liberated. Titanium carbide is a compound which is very stable and sparingly volatile. Quantitative determination of oxygen in titanium was carried out on an apparatus of the GEOKhI type [7]. The weight of test sample was 100-200 mg. By working with crucibles with $d_{ext.} = 16$ mm, $d_{int.} = 11$ mm, and $h = 40$ mm it was possible to analyze up to 600-700 mg of titanium. When larger crucibles can be used the amount of titanium can be increased.

TABLE 1

Determination of Oxygen in Titanium

Sample number	Hydrogen found		Oxygen found		Oxygen found by the chloride method, in wt. %
	in weight %	Mean	in weight %	Mean	
355/643	0.0045 0.0046 0.0046	0.0046	0.24 0.26 0.26	0.26	—
1	0.30 0.24 0.36	0.30	0.09 0.11 0.10	0.10	0.13
19	0.35 0.45 0.29	0.36	0.10 0.07 0.08	0.08	0.07
28	0.56 0.47 0.40	0.48	0.10 0.11 0.08	0.10	0.15 and 0.10
955	0.31 0.42 0.34	0.36	0.07 0.06 0.07	0.07	0.06 and 0.05
2414	0.0035 0.0033	0.0034	0.086 0.084	0.0085	—
2415	0.0058 0.0071	0.0065	0.205 0.181	0.193	—
2416	0.0090 0.0094	0.0092	0.190 0.194	0.192	—
2417	0.0055 0.0057	0.0056	0.174 0.180	0.177	—
2418	0.0024 0.0026	0.0025	0.098 0.074	0.086	—

Extraction of the gases from samples was carried out in two stages: first at a temperature of 1000° for 5 minutes, and then at a temperature of 1850° in the course of 30 minutes. There was no need to analyze the gases evolved at 1000° for their composition, since it was established in numerous tests that at this temperature only hydrogen is evolved. During the second stage, carbon monoxide was mainly evolved together with small amounts of hydrogen as impurity. The amount of hydrogen liberated at this stage was added to the amount of hydrogen liberated at 1000°. When extraction was complete, the temperature of the crucible was raised to 2100° in order to prepare the crucible for the next sample. This second calcining of the crucible did not exceed 30 minutes.

Ten samples of titanium were analyzed on the apparatus described earlier [7]. Samples No. 355/643, 2415, 2416 and 2417 were solid titanium, while samples No. 1, 19, 28, 959, 2414 and 2418 were titanium powders. The results obtained are given in Table 1.

Comparison of the results obtained show that oxygen is comparatively uniformly distributed in each sample (the small deviations in two or three determinations can obviously be related to experimental error). The same is also true of hydrogen in samples No. 355/643, 2414, 2415, 2416, 2417 and 2418 which only contain very small amounts of hydrogen which is uniformly distributed. It is also clear from Table 1 that the amount of hydrogen in samples No. 1, 19, 23, and 955 is approximately double the order in the remaining samples. Comparison of the results obtained for oxygen by the vacuum fusion method and by the chloride method, show that, within the limits of experimental errors, they are in good agreement (Table 1).

The amount of oxygen found in all samples and of hydrogen in solid titanium is proportional to the sample weight. Even when equal weights of the same sample were used in the case of the powdered titanium the hydrogen content varied very widely.

There is no doubt that all the hydrogen was completely removed, since, as indicated already, hydrogen whether dissolved or chemically combined, is readily removed on heating titanium to 1000°. That all the

TABLE 2

Replicate Determination of Oxygen in Two Titanium Samples

Sample No. 355/643 Oxygen, in % wt.	Sample No. 1 Oxygen, in % wt.
0.24	0.09
0.26	0.09
0.26	0.10
0.28	0.12
0.27	0.11
Mean 0.26 ± 0.01	0.10 ± 0.007
Mean square error 4%	7%

oxygen contained in the titanium was removed completely under the conditions we chose, was demonstrated by the facts that: 1) the analytical results we obtained are in good agreement with the results obtained by the chloride method; 2) increasing the temperature from 1850 to 2000° did not lead to an increase in the amount of liberated oxygen.

Five determinations of oxygen were carried out under the same conditions on the same sample (Table 2).

The mean square error amounts to 6%. For series analyses where, obviously, two or three determinations of the gases in titanium are sufficient, the experimental error does not exceed 10%.

The technique developed permits determination of more than 1×10^{-4}% of hydrogen and 5×10^{-3}% of oxygen in titanium.

SUMMARY

A vacuum fusion method in which coarse graphite powder is used, has been applied for the determination of hydrogen and oxygen in titanium.

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THE USE OF LABELLED ATOMS FOR STUDYING THE VOLATILIZATION OF CRYSTALLOPHOSPHOR ACTIVATORS DURING CHARGE IGNITION*

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The illumination of crystallophosphors depends to a very large extent on the activator added to the phosphorus. During the production of many crystallophosphors, the activator is added to the melt in extremely small amounts (from 1×10^{-6} to 1×10^{-3} g/g of melt). During ignition of the melt for the formation of the crystallophosphor some of the activator volatilizes. There are some semi-quantitative indications in the literature of a large change in activator concentration during ignition in alkaline-earth phosphors, for Mn about 20-25%, Bi* 50%, Cu about 30%, and Ag about 30% [1]. Consequently it can be assumed that the concentration of the activator as laid down in the formula expressing the composition of the luminophors, does not correspond to the actual concentration of the activator in the finished phosphor. A knowledge of the true concentration of the activator in the finished phosphor is however of essential importance for solving many theoretical questions, for example, for studying the formation of the localization centers of the electrons, for establishing the relation between activator concentration and the values of the light sum accumulated by the phosphors, etc.

Determination of the activator content of a phosphor by chemical analysis is extremely difficult. Consequently, in order to determine activator loss during ignition of the phosphor, we used labelled atoms. Recently, different variants of the method of labelled atoms have been used for establishing the distribution of rare earth element activators between the melt and the base in flaring phosphors [2-6], and for the determination of the copper and chloride content of phosphors based on zinc sulfide [7-9]. In our investigations we used as an activator for addition to the phosphor, an element containing a radioactive isotope. The volatility of the activator in the luminophor was then established by following the volatility of its radioactive isotope. The latter was determined on the basis of changes in γ-radiation intensity of the radioactive isotope in the phosphor measured before and after calcining. γ-Ray intensity was measured with an impulse counter. The relative intensity of the radiation was expressed as the number of impulses/minute. A comparison of the number of impulses obtained by measurement of the γ-radiation of the phosphor before and after calcining, indicates the percentage volatilization of the radioactive isotope. For both measurements the phosphor was placed in a crucible. After calcining, the phosphor decreased in volume considerably as compared with the volume of charge, and was often located unsymmetrically with respect to the vertical axis of the crucible. In order to cut down the geometrical error, the crucible containing the phosphor was rotated by means of a special apparatus, while the distance of the crucible from the tube was made large (50 cm). A lead screen (d = 3 mm) was used for filtering β-radiation. A correction for the natural background of the counter was applied to each individual measurement. The accuracy of a single determination was not less than 1%.

Homogeneity of the charge used for preparation of the phosphor was ensured by continuously mixing the moistened mass during its direct drying in the crucible to be used for calcining the phosphorus, instead of triturating the mixture as is normally done. A number of phosphors were prepared in the normal way for comparison.

Results are given below for the loss of the appropriate activators as a consequence of volatilization during calcining, Zn^{65}, Ag^{110} and Sb^{124} being used.

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* The work was carried out in 1950.

1. Experiments to establish the loss of Zn^{65} during calcining were carried out with $ZnS \cdot Zn \cdot Cu\ 5 \times 10^{-5}$ phosphors. The Zn^{65} isotope was added to the charge in the form of an aqueous solution of $ZnCl_2$. Calcining took 15 minutes. At a calcining temperature of 1000° and using the melts NaCl (5%), $MgCl_2$ (5%), $BaCl_2$ (5%), and $BaCl_2$ (25%) the following mean losses were found: 1.1 ± (0)%; 4.4 ± 0.6%; 5.2 ± 0.7%; 4.3 ± 0.7%. Thus, changes in the nature of the melts and in their amounts (about 5%) did not show any essential effect on the loss of zinc. On increasing the calcining temperature to 1100 and 1200°, and using a melt of 5% NaCl, the increases in the amount of zinc lost were 6.8 ± 1.0 and 8.2 ± 1.4%.

2. Experiments with Ag^{110} were mainly carried out with zinc sulfide phosphors. Silver was added as an aqueous solution of $AgNO_3$. The relationship between the volatility of silver and calcining temperature (from 800 to 1200°) was established, as well as the relationship between duration of calcining of the phosphor (from a few minutes to 2 hours at 1100°) and activator concentration (10^{-3}, 10^{-4}, 2×10^{-5} g/g).

a) The relationship between volatility and temperature was studied using the phosphor $ZnS \cdot Ag \cdot NaCl$ (5%); duration of calcining 30 minutes. Samples prepared in crucibles by the modified method (see above) were studied at an Ag concentration of 2×10^{-4} g/g (series I), as well as samples prepared by the normal method at an Ag concentration of 1×10^{-4} g/g (series II).

TABLE 1

Loss of Ag as a Function of Calcining Temperature for the Phosphor $ZnS \cdot Ag$, in %

Series	Temperature, in °C				
	800	9000	1000	1100	1200
I	1.4	0.8	1.5	3.8	3.8
II	—	—	2.8	5.4	12.0

TABLE 2

Loss of Activator During Calcining as a Function of the Duration of Calcining of $ZnS \cdot Ag$ Phosphors, in %

Series	Time, in minutes						
	2	5	10	15	30	60	120
I	0.6	3.5	2.7	3.7	5.4	5.0	4.7
II				1.8	3.8	6.0	

The results given in Table 1 show that the volatility of silver in ZnS phosphors increases appreciably on increasing calcining temperature above 1000°.

b) Volatility of Ag as a function of duration of calcining was studied by means of the phosphor $ZnS \cdot Ag \cdot NaCl$ (5%); calcining temperature 1100°. The phosphors were, in the main, prepared by the normal method (series I Ag 1×10^{-4} g/g) and some in crucibles (series II Ag 2×10^{-4} g/g).

The results given in Table 2 show that the decrease in activator concentration mainly occurs at the beginning of calcining. On heating for a further period, the change in activator concentration slows down.

c) For studying the relationship between loss during calcining and activator concentration, ZnS • Ag phosphors were calcined at 1100° for 30 minutes. Three activator concentrations were used Ag: 2×10^{-5}, 1×10^{-4}, and 1×10^{-3} g/g. The following values were found for the losses: 5.9, 2.0, and 6.0%.

Thus change in Ag concentration from 2×10^{-5} to 1×10^{-3} g/g has no appreciable effect on the volatility of the Ag.

d) For comparing the volatility of silver in ZnS phosphors with the volatility of silver in alkaline-earth phosphors, Sr • S • Ag 1×10^{-4} Na_2SO_4 (5%) phosphors were prepared, and calcined for 30 minutes at 1100°. A similar result was obtained: the mean loss was 4.3 ± 0.3%.

3. Antimony compounds volatilize readily even at low temperatures. Consequently in preparing luminophors with Sb as an activator it is recommended that excess of this element be taken.

During a study of the loss of Sb by the method of labelled atoms, it was shown that antimony behaves differently in different phosphors.

a) In alkaline earth phosphors the loss of antimony was determined as a function of its concentration in the charge, and as a function of calcining temperature. Duration of calcining was 15-30 minutes.

TABLE 3

The Relation Between Loss of Antimony Activator During Calcining of SrS • Sb Phosphors and Antimony Concentration, and Loss of Antimony as a Function of the Calcining Temperature of the Phosphor

Temperature in °C	Sb concentration, in g/g				
	$3 \cdot 10^{-4}$	$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$1 \cdot 10^{-1}$
700	—	—	—	—	4.3
800	—	—	—	—	3.7
900	—	—	—	—	8.4
1000	4.4	4.0	2.4	5.4	9.5
1100	9.7	7.3	—	—	—

From Table 3 it is evident that the loss of antimony during calcining of the phosphor does not change within the concentration range 3×10^{-4}-5×10^{-2} g/g. Calcining at 1000° for 30 minutes leads to losses of 4-5%; at antimony concentrations of 1×10^{-1} g/g, its volatility increases. Increasing the temperature to 1100° also increases the volatility of antimony significantly. The material obtained when a charge with this composition was calcined did not luminesce.

b) In the phosphor CaO • Sb • CaF_2 (2%), at a temperature of 1100° and antimony concentrations of 1×10^{-3}, 1×10^{-2}, and 1×10^{-1}, up to 2% of the antimony volatilizes.

c) A totally different result was obtained on calcining apatites. In these cases from 65 to 100% of the antimony contained in the charge volatilized.

Chloride ions show a considerable influence on the volatility of antimony in apatites. Phosphors with a low chloride content lost 65-75% on calcining for 30 minutes; phosphors containing a known excess of chloride lost 90-100% of their antimony under the same conditions.

In conjunction with T. S. Dobrolyubskaya experiments were carried out to establish the loss of antimony in apatites during calcining, in relation to the temperature and duration of calcining, and also as a function of the amount of charge taken. Increasing the calcining temperature from 900-1000° leads to a certain increase in antimony loss. Changes in duration of calcining from 5 to 60 minutes (at 1150°) show no effect; the antimony loss remains constant about 80%.

The loss in antimony which occurs during calcining drops significantly on increasing the amount of charge being calcined. Samples were prepared containing 3, 6, and 15 g of charge and calcined at 1150° for 15 minutes. The 3 g charge lost about 80% Sb, the 6 g charge lost 75% Sb, while the 15 g charge lost 50% Sb.

Despite the fact that the antimony was always introduced as the readily volatile compounds SbOCl and Sb_2O_3 to the alkaline-earth phosphors, and to the calcium oxide and apatite phosphors, the antimony loss in the first two phosphors on calcining was approximately one tenth of the loss in the case of apatite. Presumably, nonvolatile antimony compounds are formed in the alkaline-earth and calcium oxide phosphors, during calcining.

SUMMARY

Using labelled atoms a method has been developed for determining the amount of activator which volatilizes during calcining of phosphors. It has been found that during calcining of phosphors, the concentration of silver in zinc sulfide and alkaline-earth phosphors, and of zinc in zinc sulfide phosphors, does not decrease by more than 5-10%. The decrease in antimony concentration depends on the main component: in alkaline-earth phosphors this loss does not exceed 10%, and in calcium oxide it is not greater than 1-2%, while in apatite up to 80% is lost (when excess chloride ions are present, the loss amounts to more than 90%). Volatilization of activator mainly proceeds during the first minutes of calcining.

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QUANTITATIVE DETERMINATION OF MICRO IMPURITIES IN ANTIMONY BY NEUTRON ACTIVATION

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The radioactivation method of analysis, thanks to its exceptionally high sensitivity, has found wide application for the quantitative determination of various elements present as micro impurities in samples of a high degree of purity. Production of antimony of a high degree of purity is of great importance for the electrotechnical industry. In the work described here, a technique was developed for the quantitative determination of micro amounts of Ni, Co, Cu, Te, and As in antimony by the radioactivation method.

On irradiation of Ni, Co, Cu, Te, and As by a beam of slow neutrons, radioactive isotopes are formed as the result of (n, γ) reactions, and the half-life periods of these isotopes are sufficient for carrying out chemical separation and purifying the test elements, and for making radiometric measurements. The principles and technique of radioactivation analysis have been discussed in detail in the literature [1-3]. A number of papers have been published on the determination of Ni, Co, Cu, Te, and As in various materials.

Copper has been determined in amounts ranging from 10^{-4}-10^{-10} g [2-8]; cobalt in amounts of 10^{-8} g [9]; arsenic in amounts of 10^{-6}-10^{-10} g [10-13]; results have been given for the sensitivity of the radioactivation determination of various elements [14]. Under the conditions we used, the sensitivity of the determination of impurities on the basis of an induced activity in the appropriate isotopes equal to 40 fissions per second, up to the end of the irradiation, can be brought up to:

Ni^{65} (T = 2.6 hours) – 10^{-8} g
Co^{60} (T = 5.2 hours) – 10^{-8} g
Cu^{64} (T = 12.9 hours) – 3.4×10^{-10} g
Te^{127} (T = 9.3 hours) 1.2×10^{-8} g
As^{76} (T = 27 hours) 3.4×10^{-10} g

ANALYTICAL TECHNIQUE

The analytical technique consisted of the following operations: irradiation of sample and standards; addition of carrier to the test sample and dissolving the sample; chemical separation and purification of the test elements; determination of the chemical yield of carrier; comparison of the activity of sample and standards; determination of the radiochemical purity of the isolated active preparations.

The activity of the isolated preparations was measured by the usual torsion or cylindrical counters, and compared with the activity of standard samples, taking into account the corrections for the yield of carrier, and corrections of self-screening in the sample.

In order to ensure identical conditions a definite amount of carrier was added to test and standard samples, the chemical yield being taken into account.

Preparations used for activity measurements were of the same geometrical shape and dimensions, thereby ensuring equal scattering and absorption conditions in the preparations being compared. The radiochemical purity of the isolated preparations was checked by measurement of the half-life period.

During development of the present method, the efficiency of purification from radioactive impurities was checked by means of radioactive indicators.

Isolation and Purification of Test Elements

After irradiation, the antimony sample (about 1.5 g) was washed off the surface with hot HCl (1 : 1) and water, and transferred to a flask, to which was added as carrier, inactive salts of the test elements: Ni –10 mg, Co –15 mg, Cu –15 mg, Te –20 mg, and As –20 mg.

Isolation and Purification of Nickel. The sample was dissolved in aqua regia by heating on a water bath, the aqua regia being added gradually as necessary for dissolving the sample. When solution was complete, tartaric acid was added and nickel precipitated as usual as its dimethylglyoximate. The precipitate was filtered off on a porous glass filter, and washed with a hot solution of sodium acetate and water. The precipitate left on the filter was dissolved in HCl (1 : 1), and tartaric acid added; this was followed by 3 mg each of the salts of arsenic, tellurium, copper, and cobalt, and 10 mg of an antimony salt: the final solution was diluted with water and nickel dimethylglyoximate precipitated. Reprecipitation of nickel dimethylglyoximate was repeated once again. The final precipitate was filtered off, washed with hot water, and dissolved in the minimum amount of concentrated HNO_3; the solution was evaporated almost to dryness, and the residue dissolved in hot water. $Ni(OH)_3$ was precipitated by addition of a solution of KOH and bromine water.

The precipitate was filtered on a 30 mm diameter ashless filter paper and washed with hot water, it was then dried and the activity of the isolated nickel preparation determined.

After the activity measurement, filter paper and precipitate were placed in a tared quartz crucible and calcined. The calcined precipitate was washed with hot water and dried. The NiO was weighed and the chemical yield of the carrier determined.

Isolation of Copper and Cobalt. The ammoniacal solution containing antimony, copper, cobalt, arsenic, and tellurium, after removal of nickel, was heated and treated with HCl. The solution was then made alkaline again with NH_4OH; copper and cobalt were precipitated as their rubeanates by means of an alcoholic solution of rubeanic acid. The precipitate was filtered off, it was washed with hot water, and then dissolved in hot concentrated HNO_3: this solution was evaporated to dryness. The dry residue was treated with 1 ml of concentrated HCl and dissolved in 50 ml of water. In order to separate copper and cobalt from traces of antimony, arsenic, and tellurium, 20 mg of ferric chloride was added to the solution and ferric hydroxide precipitated by addition of ammonia. The precipitate was filtered off and discarded.

Isolation and Purification of Copper. To the ammoniacal solution of copper and cobalt was added HCl, so that the final solution was 0.3 N with respect to HCl. Cupric sulfide was then precipitated on heating. The precipitate was filtered off and washed, and then dissolved in hot concentrated HNO_3, the solution was filtered again; 3 mg each of antimony and cobalt salts were then added to the solution. The solution was evaporated to dryness and treated with a few drops of concentrated HCl, 10 ml of a 10% solution of tartaric acid was then added. Cuprous thiocyanate was precipitated by the normal method. The precipitate was filtered off, and washed with a solution of 1% KCNS containing some tartaric acid. The precipitate was dissolved, 3 mg each of an antimony and cobalt salt was added, and the cuprous thiocyanate reprecipitated.

The precipitate was dissolved in HNO_3 (1 : 1) and the solution evaporated to dryness, the residue was dissolved in water and $Cu(OH)_2$ precipitated by means of KOH solution, and then boiled for a few minutes.

The precipitate was filtered off on an ashless filter paper 30 mm in diameter, and washed with hot water, it was next dried and the activity of the isolated copper precipitate measured. After measurement of the activity, filter paper plus precipitate were placed in a tared quartz crucible and calcined to the oxide. The chemical yield of carrier was then determined.

Isolation and Purification of Cobalt. To the hydrochloric acid solution of cobalt, after removal of cupric sulfide, was added 3 mg each of antimony and copper, and the sulfides of antimony and copper were precipitated by means of hydrogen sulfide on heating. The precipitate was filtered off and discarded. The solution was made alkaline with ammonia and cobalt sulfide precipitated with hydrogen sulfide; this precipitate was filtered off and washed. The cobalt sulfide was dissolved in hot concentrated HNO_3, the solution filtered and then evaporated to dryness. The dry residue was moistened with a few drops of concentrated HCl and dissolved in 5 ml water.

Potassium cobaltinitrite was precipitated by the usual method. The precipitate was filtered off and washed, it was dissolved in dilute HNO_3 and the solution evaporated almost to dryness.

The precipitate was dissolved in water and $Co(OH)_2$ precipitated with KOH solution. The precipitate of hydroxide was filtered on a 30 mm diameter ashless filter paper and washed with hot water; it was then dried and the activity of the isolated cobalt preparation measured. After the activity measurement, filter plus precipitate were placed in a tared quartz crucible and calcined. The calcined residue in the crucible was washed with hot water and treated with nitric acid, excess of the latter was removed. The residues was treated with sulfuric acid and excess of the latter also removed by evaporation, the final residue was calcined for several minutes at 500°. Cobalt was weighed as $CoSO_4$. The chemical yield of the carrier was thus determined.

Isolation and Purification of Tellurium. To the solution obtained after removal of copper and cobalt rubeanates, was added 3 mg each of copper and cobalt and the rubeanates reprecipitated. The precipitate was filtered off. To the solution obtained was added an equal volume of 6 N HCl and the solution heated to the boiling point. Tellurium was precipitated with hydrazine sulfate and sulfur dioxide, completeness of precipitation being checked. The precipitate was filtered through a glass filter and washed with hot 3 N HCl and water.

This precipitate was dissolved in aqua regia, and to the solution was added 5 mg of antimony and 3 mg each of arsenic and copper. The solution obtained was evaporated to dryness and the residue dissolved in 50 ml of 3 N HCl. Tellurium was precipitated with sulfur dioxide and hydrazine on heating. The precipitate thus formed was filtered off and washed. Tellurium was reprecipitated once again with addition of antimony and arsenic. The precipitate was filtered through a special tared glass filter No. 4, 23 mm in diameter; it was washed with 3 N HCl, water, alcohol, and ether in turn. It was then dried at 105° and weighed; the chemical yield of carrier was thus determined. The activity of the isolated tellurium preparation was measured on a torsion counter.

Isolation and Purification of Arsenic. To the solution obtained after removal of tellurium was added 5 mg of tellurium; tellurium was precipitated on heating with sulfur dioxide and hydrazine. The precipitate was filtered off and discarded. To the solution thus obtained, concentrated hydrochloric acid was added so that its concentration in solution was about 6 N. 2-3 g of sodium hypophosphite was added to the solution and arsenic precipitated on heating. The precipitate was filtered off and washed with 3 N HCl and water. The arsenic was dissolved in hot aqua regia and 5 mg of antimony and 3 mg of copper added; the solution was then evaporated to dryness. The dry residue was dissolved in 50 ml of 6 N HCl. Arsenic was precipitated on heating with sodium hypophosphite. Reprecipitation was repeated once again with addition of 5 mg of antimony. The precipitate obtained was filtered through a special, tared No. 4 glass filter, 23 mm in diameter, and washed with 3 N HCl, water, alcohol, and ether, in turn.

The precipitate was finally dried at 105° and weighed to determine the chemical yield of carrier. The activity of the isolated arsenic preparation was determined on a torsion counter.

Purification of Standard Samples

Standard samples were prepared by introducing 0.1 ml of solution containing 10^{-7}-10^{-8} g of the test element into a quartz weighing bottle. 3 standards were prepared for each test element. The amount of carrier taken for the standard samples was 0.6 to 0.75 of the weight of the carrier taken for the test samples. Standard samples were subjected to two or three chemical purification operations in which sodium salts were added as a reverse carrier. The final chemical form of the standard samples used for weighing and measurement of activity was the same as that used for the test samples.

The analytical results (mean values) obtained are given in percentages in the Table

Sample number	Test element, %				
	Cu	As	Te	Ni	Co
1	$8.9 \cdot 10^{-7}$	$5.8 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$
2	$1.2 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$	$< 10^{-6}$	$< 10^{-6}$

The deviation for parallel samples did not exceed 35%. The accuracy of a determination is of the order of 10-20%.

SUMMARY

A method has been developed for the determination of small amounts of copper, nickel, cobalt, tellurium, and arsenic in antimony of a high degree of purity by radioactivation analysis.

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DETERMINATION OF SMALL AMOUNTS OF LEAD IN PURE METALS AND FERRO-ALLOYS

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Determination of small amounts of lead in pure metals, particularly in ferro-alloys, is a very complex problem. The best method of concentrating lead, which ensures its complete separation and practically complete removal from heavy metals, is acknowledged to be precipitation of lead with strontium sulfate. Formation of mixed crystals of $PbSO_4$ with $SrSO_4$ – the collector – and the good solubility of the sulfates of most metals, lead to quantitative trapping of the lead in the precipitate, and its separation from most accompanying elements. Chloride ions interfere with the precipitation, since they form complex ions $[PbCl_4]^{2-}$ with the lead; the latter do not enter into the crystal lattice of the $SrSO_4$. For getting lead into solution, most authors [1, 2] recommend fusing the precipitates of strontium and lead sulfates with sodium carbonate; this is followed by leaching the melt to get rid of SO_4^{2-} ions, and then dissolving strontium and lead carbonates in acid. Fusion, leaching, and filtration take considerable time, and washing of finely dispersed precipitates is accompanied by losses, which, of necessity, depress the value of the concentration method itself. In order to eliminate this drawback we used the capacity of $SrSO_4$ and $PbSO_4$ to dissolve in an alkaline solution of Complexon III [3] to form complex compounds ($K_{PbY^{2-}} = 18.2$; $K_{SrY^{2-}} = 8.6$). The precipitated lead and strontium sulfates are dissolved directly on the filter with a hot alkaline solution of Complexon III, and the lead determined polarographically in the solution thus obtained. In order to establish the optimum conditions for carrying out polarographic determination of lead in solutions containing Complexon III, preliminary studies were made of the polarographic characteristics of lead for various values of the acidity of the medium, and at varying Complexon III concentrations.

The stock solutions were prepared from analytical grade and pure grade materials. The stock solution of lead was prepared by dissolving lead metal, zero mark, in nitric acid: $T_{Pb} = 0.001300$ (1.3 g of Pb dissolved in 1000 ml). The Complexon III solution was prepared from the commercial product which had been recrystallized three times beforehand. The requisite pH value was obtained by means of indicators, and then accurately measured with a pH-meter using a glass electrode (tube potentiometer DP-5).

Control tests were carried out on standard samples taking into account the corrections for the blank.

Polarographic determinations were carried out on the "Geologorazvedka" SGM-8 No. 18952 polarograph, provided with a mirror galvanometer having a sensitivity of 2×10^{-9} amperes/mm/m; a capillary in which the drop was artificially forced off was used. In some cases a normal capillary was used; the constant of this capillary was $m^{2/3} \cdot t^{1/6} = 1.82$.

In alkaline media oxygen was removed from the solution by addition of dry Na_2SO_3, while in acid media it was removed by passing CO_2 through the solution.

Choice of the Optimum Conditions for the Polarographic Determination of Lead in a Supporting Electrolyte of Complexon III

Published information relating to the determination of lead in Complexon III as a supporting electrolyte is very scant. Prshibil [3] has given the half-wave potential of lead in a supporting electrolyte of 0.4 M CH_3COOH + Complexon III as −0.77 volt, and has pointed out that in a mixture of $CH_3COOH + CH_3COONa +$ + Complexon III, the lead wave disappears. Pecsok [4] notes that in the presence of the complexon, the value of $E_{1/2} > 1.2$ volt. There is no published data on the effect of pH on the value of $E_{1/2}$ in solutions containing

Complexon III. Accordingly, in order to establish the optimum conditions for determining lead in a supporting electrolyte of Complexon III, we, first of all, studied the relation between $E_{1/2}$ and the pH of the solution.

TABLE 1

Relation Between Wave Height and $E_{1/2}$ for Lead and the pH of the Medium when Complexon III is used as Supporting Electrolyte

pH	h, in mm	$E_{1/2}$, in volts	Slope
11.0	39.5	—1.21	0.084
9.0	23.0	—1.24	0.085
6.5	18.5	—1.31	0.120
4.8	39.5	—0.43	0.079
3.5	40.0	—0.40	0.055
>1	36.0	—0.36	0.034

The lead concentration in all the tests was 0.32 mg/ml; while the concentration of Complexon III was 0.4% (in the final volume). The requisite pH was obtained by addition of HCl or NaOH.

At a pH of 4.5-6.5 there is observed a sudden shift of the half-wave potential, and, at the same time, the value of the diffusion current falls (see Table 1). Apparently, at this point, there occurs a change-over from simple Pb^{2+} ions to the lead compound with Complexon III. As the pH increases, chemical polarization decreases; this is probably related to the change in composition of the complex lead compound ($PbHY^{-} + OH^{-} = PbY^{2-} + H_2O$). The ion PbY^{2} which is formed is reduced more reversibly on the dropping mercury electrode.

For studying the effect of Complexon III concentration on the polarographic characteristics of Pb^{2+} during its reduction on the dropping mercury electrode, all the conditions were kept the same as before. Measurements were carried out at pH 3, 6, and 10.0.

The experimental results which are given in Fig. 1 enable one to assume that normal reduction of Pb^{2+} occurs in acid media. Complexon III does not form a complex compound with lead, and does not affect its reduction. In neutral media (pH 6) when there is not sufficient Complexon III in solution (< 0.08%) the half-wave potential of lead is −0.5 volt, and the height of the wave gradually decreases with increasing Complexon III concentration. At a concentration of Complexon III sufficient for quantitative conversion of lead into the complex (Pb^{2+}: Complexon III $\geq 1:2$), $E_{1/2}$ shifts rapidly to more negative values. Further increases in Complexon III concentration have no effect on the value of the diffusion current and on that of $E_{1/2}$. In contrast to neutral media, where lead is found in the form of Pb^{2+} ions, formation of the complex lead ion with Complexon III in alkaline media, is connected with a break down of the PbO_2^{2-} ions. Under these conditions, increases in the concentration of Complexon III leads to practically complete suppression of the wave for PbO_2^{2-} ions. A well defined wave of the ion PbY^{2-} appears at a sufficiently high Complexon III concentration (Fig. 1); under such conditions $E_{1/2}$ for lead shifts rapidly to more negative values. Chemical polarization is considerably less in alkaline media than in neutral media (Fig. 2); this indicates a more reversible reduction process for PbY^{2-} as compared with $PbHY^{-}$.

The optimum conditions for the polarographic determination of lead are a pH of 3.5 and a Complexon concentration of 0.1%. The relation between the wave-height for lead and its concentration is linear. This permits determination of lead by the method of additions, calculations being carried out according to the formula:

$$X = \frac{h_1 a V}{h_2 (V + V_1) - h_1 V},$$

where h_1 is the wave height before addition, in mm; a is the amount of lead added in mg; V is the original volume of solution in ml; V_1 is the volume of solution added, in ml; and h_2 is the wave height after addition in mm.

Determination of Traces of Lead in Synthetic Mixtures and in Standard Samples

A 5-10 g aliquot of the sample was dissolved on heating in H_2SO_4 on the basis of about 20 ml acid to 1 g of sample. The walls of the beaker in which the sample was dissolved were washed with 20-25 ml of hot water and the whole boiled for 2-3 minutes. To the boiling solution, HNO_3 (sp. gr. 1.4) was added dropwise, until the

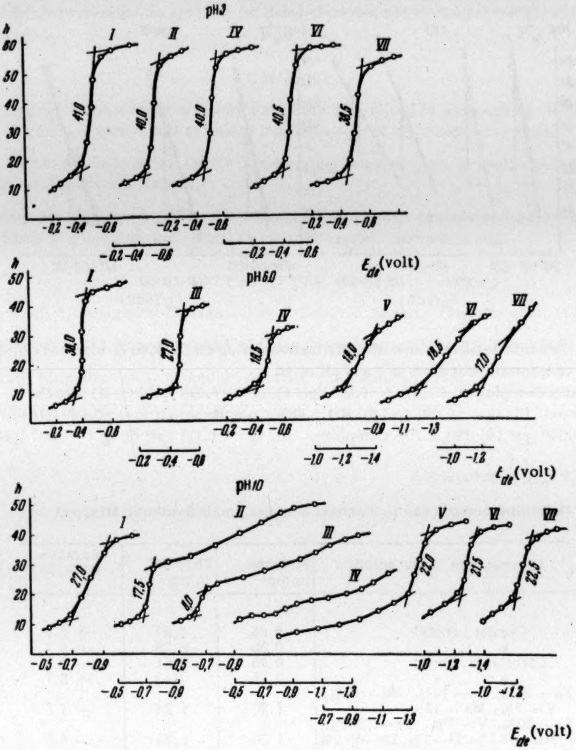

Fig. 1. Polarograms for lead in a supporting electrolyte of NaCl + Complexon III at pH's of 3, 6, and 10:
1) Without Complexon III; II) 0.008% Complexon III; III) 0.016%; IV) 0.032%; V) 0.08%; VI) 0.16%; VII) 1.6%; Complexon III.

turbulent oxidation of divalent iron was complete, the solution was then evaporated until white fumes started to appear. The salts obtained were dissolved in hot water, and the volume made up to about 200 ml. When the test sample contained less than 1% tungsten and molybdenum, lead could then be precipitated immediately. For this purpose 10 ml of a 1% solution of $Sr(NO_3)_2$ was added in small portions and the resultant mixture left to stand for 2-3 hours. The precipitate which could contain $SrSO_4$, $PbSO_4$, SiO_2, C and impurities coprecipitated with it, was filtered through a dense filter, care being taken to avoid transferring the precipitate itself on to the filter, the precipitate was then washed with 1% H_2SO_4, and washed once with hot water; it was finally dissolved in a small amount of a 3% solution of Complexon III in 2 N NaOH. The solution thus obtained was neutralized with hydrochloric acid using Methyl Orange as indicator, and transferred to a 25 ml standard flask in which it was made up to the mark with water and thoroughly mixed. 10 ml of this solution was placed in the electrolyzer and CO_2 passed through it for 2 minutes; polarograms were then taken. A standard solution of lead was added to the solution already in the electrolyzer and polarograms taken again.

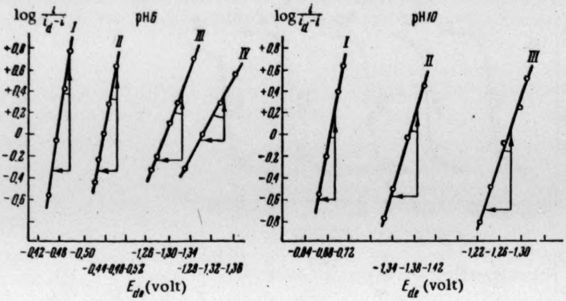

Fig. 2. Relation between electrode polarization during electrolysis of lead and Complexon III concentration at a pH of 6 and pH of 10.
1) 0.016% Complexon III, tg < −0.031 (pH 6); tg < −0.028 (pH 10); II) 0.032% Complexon III, tg < −0.038 (pH 6); III) 0.08% Complexon III tg < −0.069 (pH 6); tg < −0.049 (pH 10); IV) 0.16% Complexon III, tg < −0.111 (pH 6); tg < −0.057 (pH 10).

TABLE 2

Determination of Lead in Standard Samples and in Synthetic Mixtures

Composition of test solution	Pb taken, in mg	Pb found, in mg	Relative error, in %
Copper metal	0.65	0.67	+ 3.1
» »	0.30	0.28	— 6.7
Chromium metal	0.65	0.61	— 6.2
» »	0.45	0.48	+ 6.7
Fe — 21%, Cr — 14%, Mo — 43%, V — 7%, Mn — 14%	1.30	1.28	— 1.5
Fe — 20%, V — 7%, Cr — 13.5%, Mn — 13.5%, Ti — 1%, Mo — 40.5%	1.30	1.24	— 4.6
Nb — 1.5%, Ta — 3%, Cr — 60%, Mn — 10.2%, Mo — 3.65%, Fe — 22%, V — 4.7%, W — 1%	0.30	0.31	+ 3.3
Mo — 73%, Fe — 3.65, V — 4.9%, Cr — 9.75; W — 1%, Mn — 8.5%	0.20	0.18	—11.0
Fe — 72%, Mo — 3%, Cr — 9.6%, V — 4.8%, Mn — 8.4%, W — 2.4%	0.10	0.09	—10.0
Stand. steel samp. 164	1.30	1.30	0.0
« « « 139a	0.65	0.63	— 3.1
« « « 158	0.30	0.32	+ 6.6
« « « 159	0.10	0.11	±10.0

When the Mo, W, and V content of the test samples was very high, the analytical procedure was rather more complicated. After the sample had been dissolved and the solution obtained had been evaporated down until white fumes appeared, and the solution diluted with water to 200 ml, Ni, Fe, Cr, Mn, Pb and the other elements were precipitated with excess Na_2CO_3. The precipitate obtained, which was free from Mo, W, and V (these metals remaining in solution as the tungstate, molybdate, and vanadate) was dissolved on heating in dilute H_2SO_4, the lead was then removed from the remaining impurities as before by precipitating with $SrSO_4$.

The limiting sensitivity of the method amounts to 0.002 mg Pb/ml which corresponds to 0.001% Pb on a sample weighing 10 g. An analysis takes 3-5 hours without taking into account preliminary preparation (taking samples and getting them into solution).

The method has been checked on synthetic mixtures of copper and chromium metal, and on standard samples of alloyed steel.

SUMMARY

1. The polarographic characteristics of lead have been determined in a supporting electrolyte of Complexon III at various pH values, and at various concentrations of the complexing agent.

2. A rapid method has been developed for concentrating small amounts of lead, which excludes the operation of fusing the sulfates with Na_2CO_3.

3. A technique has been developed for the determination of small amounts of lead (of the order of 0.01-0.002%) in steels based on chromium and nickel, in metallic copper, chromium, etc.

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DETERMINATION OF LEAD SULFATE IN THE ACTIVE MASSES OF LEAD ACCUMULATORS

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The main components of the active masses of lead accumulators are the oxide, dioxide, carbonate, and sulfate of lead as well as metallic lead; the ratios of the various components vary considerably. The method which has been adopted hitherto for extracting SO_4^{2-} ions from the active mass of a lead accumulator, is based on the reaction $PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 \downarrow + Na_2SO_4$. The solubility of lead carbonate is considerably less than that of lead sulfate; this ensures that the reaction proceeds from left to right. All the same, equilibrium is only comparatively slowly established in the mixture, and in order to get consistent and reproducible results, it is necessary to heat the sample of the mass with saturated sodium carbonate solution for not less than 2 hours. The filtration and washing operation following this stage, which involve dealing with a finely dispersed precipitate that readily passes through the filter, complicate and slow down analysis. A complete analysis takes 5-6 hours. Moreover, the sodium carbonate method, while being very accurate for the analysis of synthetic mixtures of lead peroxide and lead sulfate, does not guarantee quantitative extraction of SO_4^{2-} ions for low contents of lead sulfate in the mass of positive plates.

Incomplete extraction of sulfate from the mass during boiling with sodium carbonate solution, can, in our opinion, be explained as follows. When the accumulator is charged, the lead sulfate of the anode plate is oxidized to PbO_2. The insignificant amounts of $PbSO_4$ still remaining in the mass of the anode plate of a well charged accumulator, are mainly present as very fine crystals surrounded by a dense and comparatively thick layer of lead dioxide. When even a well ground test sample is boiled with sodium carbonate, most of the lead sulfate continues to be blocked by the dense layer of lead dioxide, which prevents free diffusion of the reagent (Na_2CO_3) to the surface. The final result is incomplete transfer of SO_4^{2-} ions into solution with consequently low experimental values.

In order to determine SO_4^{2-} ions quantitatively and to speed up the treatment of the mass, we have used a cementation process. Essentially, this method consists of treating an aliquot part of the active mass of an anode plate with hydrochloric acid (1 : 1) to convert PbO_2 into $PbCl_2$, and then reducing the latter to the metal with zinc turnings. Treatment is continued until the whole aliquot dissolves and all the lead has been deposited on the zinc. When such a treatment is used, all the components of the mass are broken down, as a result of which the blocking action of PbO_2 is eliminated, and all the sulfate ions present in the mass pass into solution; the sulfate ion is then determined in the solution obtained by one of the generally accepted methods, the time necessary for treatment can be reduced to 10-15 minutes.

Various samples of the active masses of lead accumulators were analyzed by the suggested method of cementing lead on metallic zinc, and by the method in which lead sulfate is extracted by means of sodium carbonate solution. The analytical results obtained are given in Table 1.

As the results in Table 1 show, percentage extraction of lead sulfate by sodium carbonate solution decreases with decreasing lead sulfate concentration.

The following series of experiments were carried out in order to show that at low lead sulfate concentrations, most of the lead sulfate still remains in the filtered precipitate after the sodium carbonate extraction.

TABLE 1

Determination of Lead Sulfate in Active Masses by the Cementation and Sodium Carbonate Methods

Analytical method	Lead sulfate found, in %										
Cementation of lead on metallic zinc	65.6	40.3	21.3	17.1	10.2	5.46	2.20	2.55	2.10	1.79	1.95
Sodium carbonate method	65.4	40.3	20.8	16.2	8.6	3.56	0.34	0.14	0.11	0.05	None
Percentage of sulfate extracted by the sodium carbonate method	99.7	100	97.6	94.7	84.3	65.2	15.5	5.5	5.2	2.7	0

TABLE 2

Determination of Lead Sulfate in Active Masses at Low Lead Sulfate Contents

Method of treatment and test material	Lead sulfate found, in %						
Sodium carbonate treatment of the active mass	14.1	4.23	3.34	0.51	0.47	1.60	1.46
Acid treatment of the filtered precipitate	2.1	1.08	1.17	2.67	2.73	0.92	1.14
Total	16.2	5.31	3.51	3.18	3.20	2.52	2.60
Acid treatment of the active mass	16.0	5.20	3.47	3.29	3.34	2.51	2.63

TABLE 3

Determination of Lead Sulfate in Active Masses by the Sodium Carbonate and Acetate Methods

Test number	$PbSO_4$ found, in %		Deviation, in %	Test number	$PbSO_4$ found, in %		Deviation, in %
	sodium carbonate method	acetate method			sodium carbonate method	acetate method	
138	17.8	17.8	—	443	18.9	18.8	−0.1
139	26.2	26.4	+0.2	481	34.9	34.2	−0.7
140	35.8	35.7	−0.1	482	21.2	21.3	+0.1
141	41.8	42.3	+0.5	483	20.6	20.9	+0.3
380	62.4	62.3	−0.1	484	58.4	58.0	−0.4
381	39.9	40.3	+0.4	485	35.3	35.0	−0.3
382	22.6	22.6	—	486	21.7	21.8	+0.1
383	21.0	21.2	+0.2	487	16.1	16.1	—
441	33.7	33.2	−0.4				
442	19.8	19.9	+0.1				

A number of active masses from the positive plates of well charged accumulators (low lead sulfate content) were treated with saturated sodium carbonate solution at the boiling point for 4 hours. The precipitates were filtered off and washed with hot water. SO_4^{2-} ions were determined gravimetrically in the solution plus wash liquors. Precipitate and filter were then treated with hydrochloric acid (1 : 1) to convert the lead dioxide into the chloride, the latter was then reduced to the metal with zinc turnings. SO_4^{2-} was determined gravimetrically in the solution remaining after removal of the lead.

In parallel tests, the lead sulfate was determined by the suggested method of decomposing the aliquots with hydrochloric acid, followed by cementation of the lead with zinc.

The results obtained (Table 2) show clearly that the sodium carbonate method is not applicable for extraction of sulfate ions from the mass when the sulfate content is low.

The acid treatment of the mass of a positively charged plate, in addition to cutting down the time of analysis, ensures quantitative transfer of sulfate ions into solution.

The main components of the active masses of negatively charged plates are Pb, $PbSO_4$, and $PbO(PbCO_3)$, the lead sulfate content of the mass, as a rule, amounts to not less than 10-15%. Under such conditions, the sodium carbonate treatment for lead sulfate determination gives fully satisfactory results; all the same the length of treatment led us to use the cementation method in these cases as well.

We used an acetate mixture consisting of equal volumes of 5 N CH_3COOH and 5 N CH_3COONH_4 to dissolve the main components of the mass.

Working with an acetate mixture eliminates foaming of the solutions in the presence of organic additives in the masses, and ensures rapid and quantitative reduction of lead by zinc. The low acidity of the solution (pH about 4) leads to minimum expenditure of zinc as a result of hydrogen liberation, while the buffer properties of the mixture prevent hydrolysis of zinc salts during washing of the precipitate of spongy lead. Treatment of the mass does not exceed 10 minutes.

Results of determinations by the acetate method are given in Table 3.

Procedure. 3 g of well ground mass was placed in a 150 ml beaker and 15 ml of solution added (for positive masses HCl 1 : 1; for negative masses, equal volumes of 5 N CH_3COOH and 5 N CH_3COONH_4). The contents of a beaker were brought to the boil and then boiled for 2-3 minutes (in a forced draft) with constant stirring. 25 ml of distilled water was then added, followed by a heap of zinc turnings 1-2 g. The solution was boiled until the whole mass had dissolved and lead had been quantitatively deposited on the zinc. The absence of a grey coating on a fresh strip of zinc introduced into the solution, testified to complete reduction of lead. The heap of spongy lead with zinc residues was then packed with a glass rod and washed with decantation, and finally discarded. Sulfate ions were then determined by one of the conventional methods. Results were calculated in terms of $PbSO_4$.

This method has been adopted in the laboratory of the Scientific Research Accumulator Institute.

SUMMARY

1. It has been shown that the sodium carbonate method of determining lead sulfate in the active masses of lead accumulators is inapplicable when the lead sulfate content is low.

2. A new method is suggested for getting $SO_4^{=}$ ions into solution during determination of lead sulfate in active masses.

3. An acid treatment of positively charged masses, and an acetate treatment of negatively charged plates, with subsequent cementation of lead on zinc, is recommended.

4. The suggested method cuts down the time required for determination of $SO_4^{=}$ to a quarter or a fifth of the time taken in the previous method.

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DETERMINATION OF CHLORINE DIOXIDE IN SOLUTION

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According to published results [1-5], bleaching of cellulose and cloth by chlorites is most effective in an acid medium ($pH < 5$). At the same time, it is known that appreciable amounts of chlorine dioxide are formed in acid solutions of chlorites [6, 10-13], the amount formed being greater the more acid the medium. It has not yet been made clear whether bleaching in acid solutions of chlorites is the result of the action of chlorine dioxide alone, or whether it is a combination of chlorine dioxide and chlorite [6-10]. On the other hand, during bleaching by means of chlorine dioxide in weakly acid, neutral, or weakly alkaline media, certain amounts of chlorite may be formed.

Thus, bleaching can often be realized when chlorine dioxide and chlorites are present together in bleaching solutions. The rate and intensity of these processes will depend on the ratio of these materials. Consequently, simultaneous analysis of chlorine dioxide and chlorites in bleaching solutions is necessary for controlling the bleaching process.

A method has been published for the determination of chlorine dioxide which is based on its interaction with alkalis:

$$2ClO_2 + 2OH \rightarrow ClO_3 \rightarrow ClO_2^- + H_2O.$$

The end point of this analytical reaction is usually established visually – on the basis of the decolorization of the yellow-green solution. Nevertheless, during a study of this method, we established, in the first place, that decolorization of the solution, even in a strongly alkaline medium, does not occur immediately, and secondly, that decolorization is not an objective criterion for assessing the practically complete conversion of chlorine dioxide.

In our experiments we used freshly prepared solutions of chlorine dioxide, which were obtained from chemically pure (analytical grade) potassium chlorate and oxalic acid in the dark. Before absorption with twice-distilled water, the chlorine dioxide was compressed to free it from impurities present in the form of other gases (mainly from CO_2). The solutions were stored in flasks made from dark glass and stoppered with ground glass stoppers wrapped in black paper.

Exactly measured volumes of the same sample of test solution were introduced into two conical flasks fitted with ground glass stoppers. The first flask contained a mixture of acid and potassium iodide, while the second contained a solution of sodium hydroxide of equal concentration.

After the test solution had been introduced into the flasks, the latter were stoppered. After 5 minutes the iodine liberated in the first flask was titrated with sodium thiosulfate. The second flask was stored in the dark. Periodically, the color of this solution was observed. As soon as decolorization was observed, the test solution was poured into an acidified solution of potassium iodide and the iodine liberated then measured.

Some of the results obtained during these experiments are given in Table 1.

In twenty-six of the thirty-six experiments we carried out, the amount of active chlorine expressed in gram-equivalents which was found, was more than 40% of the initial amount of chlorine dioxide.

TABLE 1

Chlorine dioxide in the sample of solution taken, in gram equivalents	Sodium hydroxide content of the original solution, in gram equivalents	Active chlorine content in solution after decolorization, in gram equivalents	Ratio of gram equivalents of active chlorine in the solution after decolorization to gram equivalents of chlorine in the original solution	Gram equivalents of active chlorine amounting to 40% of the original value
0.001140	0.01600	0.000470	41.2	0.000455
0.001250	0.01600	0.000502	40.2	0.000500
0.001530	0.01600	0.000640	41.8	0.000610
0.001905	0.01600	0.000800	41.9	0.000760
0.002050	0.01600	0.000830	40.5	0.000820
0.001760	0.00400	0.000680	38.6	0.000705
0.001140	0.00400	0.000451	39.6	0.000456
0.000880	0.00200	0.000350	39.8	0.000352
0.000745	0.00100	0.000290	38.9	0.000298
0.001320	0.00300	0.000505	38.4	0.000528

In ten cases – those in which the amount of sodium hydroxide taken was in relative small excess of that required for reacting with chlorine dioxide – the amount of active chlorine, expressed in gram equivalents found was less than the amount which corresponds to the equation for the reaction. It is possible that these last results were caused by side decomposition of chlorine dioxide during the time of the experiments, since, in these cases, decolorization usually occurred after one hour. The experimental results rarely coincided, within the limits of possible errors, with the values one would expect on the basis of theoretical considerations.

It might be thought that it should be possible, by establishing certain conditions, to ensure that the course of the decomposition of chlorine dioxide follows the equation given above. Nevertheless, even if it were possible to do this, there is still no objective criterion for establishing that the reaction has practically gone to completion, since the visual method cannot, under any circumstances, be regarded as reliable for determining the end point. In addition, the comparatively slow reaction rate means that a technique based on it will not be suitable for production control of the bleaching process. Control of the composition of bleaching solutions under production conditions must be based on reactions which are rapid, and whose end points are readily established. In this connection our attention was drawn to the reaction between chlorine dioxide and peroxides, which has been known for a long time [14, 15]:

$$2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2;\ 2ClO_2 + 2HO_2^- \rightarrow 2ClO_2^- + {}^3/_2\ O_2 + H_2O.$$

This reaction is used for preparation of chlorites; it proceeds instantaneously in alkaline solution. From this point of view it should prove most convenient for use under production conditions.

It should be explained that this reaction is not complicated by side reactions, which would interfere with its use in analysis. To demonstrate this, two series of experiments were carried out: in one of these, determinations were made of the amount of active chlorine remaining after decomposition of pure chlorine dioxide by means of hydrogen peroxide in an alkaline solution, and after removal of excess hydrogen peroxide, by boiling the solution. In the other series of experiments, a study was made of the reaction between chlorite and hydrogen peroxide in an alkaline solution, under the conditions used for analysis. Freshly prepared solutions of chlorine dioxide free from chlorates, chlorides, and chlorine were used in the first series of experiments.

The technique used for selecting test samples was the same as in the experiments with alkali. The central part of the solution of chlorine dioxide taken by means of a pipet was divided into three parts which were introduced into three flasks: in the first flask ClO_2 was determined iodometrically; in the second flask chlorine dioxide and chlorates were determined by means of ferrous sulfate and permanganate; while in the third flask, the chlorine dioxide was decomposed with hydrogen peroxide in alkaline solution, after which, chlorite was determined iodometrically.

The original solutions of chlorine dioxide were free from chlorates, consequently, the analytical results for the first and second flask coincided.

TABLE 2

Chlorine dioxide content of the test solution, in gram equivalents (iodometrically)*	Chlorite content after decomposition, in gram equivalents (iodometrically)	Ratios of gram equivalents of chlorite and chlorine dioxide, in %	Notes
0.000325	0.000265	81.5	The chlorine dioxide solution was obtained by preliminary compression of the gas
0.000385	0.000315	81.8	
0.000455	0.000365	80.2	
0.000540	0.000430	79.6	Freshly prepared solutions were analyzed
0.000785	0.006630	80.3	
0.001645	0.001315	79.9	
0.000885	0.000705	79.6	The solutions were prepared by dissolving the gas which had not been compressed beforehand
0.001665	0.001325	80.0	
0.002325	0.001855	79.8	
0.002840	0.002280	80.3	Freshly prepared solutions were analyzed
0.003565	0.002845	79.7	

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* 0.1 N sodium hydroxide was used; the pH of the test solution varied within the limits 10-10.5.

TABLE 3

Chlorite content of original solution, in gram equivalents (iodometrically)	Amount of 3% hydrogen peroxide	Boiling time, in minutes	Chlorite content of test solution after boiling, in gram equivalents (iodometrically)	Notes
0.000700	4 drops	5	0.000695	Analysis of the solution was carried out the first time immediately the solution was cool, while the second time it was analyzed 5 hours after cooling
0.000700	None added	5	0.000700	
0.000700	8 drops	5	0.000695	
0.001135	5 drops	5	0.001140	Analysis carried out immediately after cooling
0.001400	None added	5	0.001395	
0.001400	3 drops	5	0.001390	The same
0.001400	16 drops	5	0.001385	The same
0.002285	3 drops	5	0.002290	The same
0.002285	3 drops	5	0.002290	The same
0.001140	3 ml of 33% hydrogen peroxide solution	20	0.000985	The same

The amount of hydrogen peroxide necessary for decomposing the chlorine dioxide was determined beforehand, so as to avoid any appreciable excess of peroxide which would be difficult to get rid of. The amount of hydrogen peroxide taken was such that it was present in excess only to the extent of one or two drops of 3% solution. This excess amount is readily destroyed by boiling the alkaline solution for 5 minutes, and, as special tests showed, this destruction of hydrogen peroxide has no effect on the chlorite. When the solution was cold, cooling being accelerated by means of cold tap water, chlorite was determined in it iodometrically. The results of this series of experiments are given in Table 2.

It is evident from the results given in Table 2 that in most cases, the values obtained were satisfactory. The inaccuracy increases when the amount of chlorine dioxide taken is too small.

In order to carry out an analysis, it is necessary to take samples whose chlorine dioxide content is in excess of 0.000500 gram equivalents.

Analysis is possible when chlorite, chlorate, chloride, and carbonates are all present simultaneously.

An analysis usually takes 7-10 minutes. In order to confirm that the method we suggest is reliable, a series of experiments was carried out to study the interaction of chlorite with hydrogen peroxide under the conditions used for analysis, particularly when the solution is boiled. In these experiments, various amounts of hydrogen peroxide were added to an alkaline solution of chlorite of known concentration. Each aliquot of solution was boiled, and, after cooling, chlorite was determined iodometrically. Results of these experiments are given in Table 3.

It is clear from these results that a small excess of hydrogen peroxide, amounting to 3-8 drops of the 3% solution, does not lead to appreciable decomposition of an alkaline solution of chlorite (pH about 10.5-11.0) on boiling for 5 minutes.

A larger excess of hydrogen peroxide and a longer boiling time may lead to appreciable decomposition of chlorite.

SUMMARY

A method which is suggested for the analysis of chlorine dioxide in solution is based on its decomposition with hydrogen peroxide in an alkaline medium.

The method is suitable for the determination of chlorine dioxide in the presence of chlorite, chlorate, chloride, and carbonates; it can be used for the simultaneous determination of chlorine dioxide and chlorite in bleaching solutions.

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PHOTONEPHELOMETRIC DETERMINATION OF CAFFEINE

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Quantitative determination of caffeine, particularly small amounts of it, presents certain difficulties. Methods for the quantitative determination of pure preparations of caffeine are not given in the State Pharmacopeia (Eighth Edition). A number of methods have been published for quantitative determination of caffeine in various objects.

Markovnikov [1] suggested an original method for the quantitative determination of caffeine in tea, which was based on the decomposition of the compound of caffeine with tannic acid by magnesium oxide, and evaporating the aqueous solution of the free caffeine to dryness, and then extracting the caffeine from the residue with benzene in a special apparatus. Markovnikov found 2.44% of caffeine in Kubeisk tea.

Borodin, using Markovnikov's method, determined caffeine in cake [2], and kiln tea [3], and found 2.76% of caffeine in the former and 2.44% in the second.

A number of methods have been developed for the quantitative determination of caffeine in medicinal preparations [4-8].

Soboleva [9] has made a review of the literature on the determination of caffeine and other purine derivatives.

Methods of determining caffeine in plant material have been described in papers on the biochemistry of tea [10] and on the biochemistry of tea production [11].

Determination of small amounts of caffeine is of great practical importance for tea production, for preparing pure caffeine preparations, and for controlling finished medicinal products.

Conditions for Precipitating Caffeine and Construction of a Calibration Curve

Of the many well known alkaloid precipitants which we tested, the only one which proved to be suitable for obtaining a nephelometric turbidity with caffeine, was phosphotungstic acid [12].

On the basis of preliminary experiments we adopted a definite sequence for mixing the solutions, their optimum concentrations were established, as well as the time of standing after adding the reagents before nephelometric determinations can be made.

Into a conical flask was introduced in succession a 0.01 M solution of sodium phosphotungstate, 2.5 M nitric acid, 0.0001 M caffeine solution, and distilled water in amounts to ensure that the galvanometer reading was a maximum and was stable.

For our work we used a photonephelometer of the system proposed by V. E.Nize; this was a differential setup with selenium vapor photoelements, issued by the Leningrad Electrotechnical Institute. The photoelements were type K- 10 with a sensitivity of 550 micro amperes per lumen and an emf of 170 millivolt. A "Multiflex" mirror galvanometer was connected in parallel with the photoelements; this mirror has a scale with 100 divisions, and a sensitivity of 1×10^{-8} amperes/mm; variations of the voltage in the circuit within the limits 80-180 volts were stabilized with a ferroresonance stabilizer with a power of 5 watts.

It is evident from Table 1 that for a constant amount of caffeine in the reaction mixture, and for a constant volume* of the latter, equal to 50 ml, the readings of the galvanometer had their maximum value after 10 minutes, when the reaction mixture contained 2 ml of sodium phosphotungstate and 4 ml of nitric acid.

Subsequently we established that for certain concentration limits of the caffeine, the number of milliliters of sodium phosphotungstate solution and nitric acid added to the reaction mixture could be kept constant; this simplified experimental procedure.

TABLE 1

Taken, in ml				Galvanometer readings after the time intervals given in minutes			
0.01 M sodium phosphotungstate solution	2.5 M nitric acid	0.001 M caffeine*	Distilled water	2	4	10	20
1	4	2	43	30	40	40	42
2	4	2	42	50	56	63	63
3	4	2	41	45	58	60	63
3	3	2	42	42	50	52	50
3	5	2	40	32	36	40	40

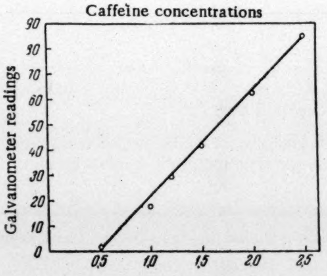
* 1 ml of reaction mixture contained 7.76 γ of anhydrous caffeine.

The experimental procedure adopted consisted of the following in all cases.

Using a micropipet, the following solutions were introduced in succession into 50 ml flasks: 2 ml of a 0.01 M solution of sodium phosphotungstate, 4 ml of 2.5 M nitric acid, and known amounts (0.5, 1.0, 1.5, 2.0, and 2.5 ml) of a 0.001 M solution of caffeine; these solutions were carefully mixed and made up to the mark with distilled water, the solutions were finally transferred to 100 ml conical flasks, mixed again, and then nephelometrically determined.

On the basis of the galvanometer readings obtained after 5 minutes, a calibration curve was constructed using five points (diagram).

When the calibration curve was used the experimental error did not exceed 5%.



The number of mls of 0.001 M caffeine solution in the reaction mixture (1 ml of 0.001 M caffeine solution corresponds to 3.88 microgram of anhydrous caffeine in 1 ml of reaction mixture) is plotted on the ordinate.

Using the calibration curve we determined the caffeine content of tea leaves obtained from a plantation, and of medicinal products prepared in pharmacies and in the laboratory. The work was carried out with periodic control of the apparatus by means of a standard turbidity. The calibration curves do not have to be checked more than once a month.

All calculations were made on the basis of anhydrous caffeine, assuming a moisture content of 8.5% in the sample.

Quantitative Determination of Caffeine in Tea Leaves

The caffeine content of tea leaves, according to various results [13], varies from 1 to 4.8% according to the type of tea. Caffeine can be extracted completely from plant material by means of hot water.

In order to ascertain whether or not it is possible to carry out a nephelometric determination of caffeine

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* The volume was chosen to suit the dimensions of the photonephelometer cell.

TABLE 2

Taken, in ml					Number of micrograms of anhydrous caffeine in 1 ml of the reaction mixture taken	No. of micrograms of anhydrous caffeine found in		Relative experimental error, in %
0.01 M sodium phosphotungstate solution	2.5 M nitric acid	Test extract	0.001 M caffeine solution	Distilled water		1 ml of reaction mixture by using the calibration curve	100 ml of extract, or in the aliquot taken, in %	
2.0	4.0	None	1.0	43.0	3.88	3.71	None	—4.9
2.0	4.0	»	1.5	42.5	5.82	6.07	»	+4.8
2.0	4.0	»	2.0	42.0	7.76	7.59	»	—2.2
2.0	4.0	2.0	None	42.5	None	3.59	1.02	
2.0	4.0	4.0	»	40.0	»	7.59	1.08	
2.0	4.0	2.0	1.0	41.0	3.68	7.59	1.05	

according to our method, in the presence of certain materials which are characteristic of plant extracts, we made a series of tests with catechin tanning materials, gallotannin, ascorbic acid, glycocol, and cystine. Tests showed that the presence of the materials indicated above as impurities, did not interfere with precipitation of caffeine with sodium phosphotungstate in the presence of nitric acid.

Caffeine was determined in tea leaves as follows: an aliquot (1 g) of the latter, after determination of their moisture content (12%), was covered with boiling distilled water (100 ml). Caffeine was determined in the transparent, yellow-brown extract. By using the technique of adding known amounts of caffeine to the test extract, we established that it is possible to determine caffeine in plant raw material with a satisfactory degree of accuracy (Table 2).

On adding twice the volume of test liquid to the reaction mixture, the galvanometer readings obtained indicated the presence of double the amount of caffeine when the calibration curve was used; this indicates that the determination is reliable.

Quantitative Determination of Caffeine in Medicinal Products

Caffeine is used in amounts of 0.05-0.1 g in complex medicinal mixtures [14]. The following medicinal mixtures which contain sodium caffeine benzoate or pure caffeine were tested: a 10% solution of sodium caffeine benzoate in ampoules, a 20% solution of sodium caffeine benzoate in ampoules, sodium caffeine benzoate – sugar, sodium caffeine benzoate – phenacetin, caffeine – phenacetin, caffeine – luminal, caffeine – pyramidone, caffeine – antifebrin, caffeine – aspirin, caffeine – urotropine, caffeine – sodium bicarbonate – sodium salicylate, caffeine – veronal – pyramidone.

In trying to establish the possibility of determining caffeine benzoate or pure caffeine, when they are in the presence of the ingredients listed above, it was found that sodium phosphotungstate in an acid medium, only precipitates pyramidone and urotropine as well as caffeine. Pyramidone and urotropine form precipitates which dissolve on adding sufficient water. In the remaining cases, determination of caffeine went very smoothly.

The 10 and 20% solutions of sodium caffeine benzoate required for the tests were prepared according to to the Pharmacopeia from anhydrous caffeine, anhydrous sodium benzoate, sodium bicarbonate, and water (up to 1 liter). 1 ml of the solution thus prepared (or taken from ampoules) was introduced into a 50 ml standard flask and made up to the mark with distilled water. 30 ml of the solution thus obtained was made up to 100 ml with water in another standard flask; 1 ml samples of solution were taken for carrying out the determinations.

As a control, a known volume of 0.001 M solution of caffeine was added to the reaction mixture in a separate experiment, in addition to the test solution.

3.44-3.84% of anhydrous caffeine was found in the 10% test solution of sodium caffeine benzoate by the photonephelometric method; this was in agreement with the requirements of the Pharmacopeia.

A 20% solution of sodium caffeine benzoate (Pharmacopeia requirements) contained in ampoules was tested in the same way, except that in this case 0.5 ml of liquid was taken for dilution; the volume was made up to 50 ml with water. In this 20% solution of sodium caffeine benzoate, 7.05-9.97% of anhydrous caffeine was found; this also agreed with Pharmacopeia requirements.

The techniques we developed for the photonephelometric determination of caffeine in pharmacopeia injection solution was used for determining caffeine in dry medicinal preparations. Mixtures prepared in the laboratory and in pharmacies were subjected to comparative analysis.

An aliquot of the mixture (0.3 g) – sodium caffeine benzoate 0.1 g and sugar 0.2 g – was dissolved in 20 ml of distilled water, and the solution filtered into a 50 ml standard flask; it was then made up to the mark with water. 30 ml of this solution was transferred to a 100 ml standard flask, and this again made up to the mark with water; 1 ml of this solution was taken for carrying out a determination. 1 ml should contain 4.33 γ of anhydrous caffeine. The factor for converting anhydrous caffeine to sodium caffeine benzoate is 2.63.

Experiments showed that quantitative determination of caffeine in dry mixtures by the method described is fully possible, and that it gives reasonable accuracy. Experimental error did not exceed 6%; this corresponds to the norms for permissible quantitative deviations from the specified formula for a preparation [15].

Other test mixtures either dissolved completely in water as described above, or only the caffeine and sodium caffeine benzoate which they contained were dissolved.

In the latter cases, an aliquot of the test mixture (powders only) was extracted with 10 ml of distilled water and the solution obtained filtered into a 50 ml standard flask. The powder remaining was then treated a few times with small portions of water, the supernatant solution being transferred each time through the filter into the standard flask. The volume in the flask was, in this way, brought up to the mark.

Having calculated what further dilution was necessary so that 1 ml of the final reaction mixture contained approximately the amount of caffeine that could be determined by means of the calibration curve, such dilution was carried out, and 1 ml of the dilute solution thereby obtained measured out with a micro pipet and the usual nephelometric determination carried out.

Caffeine and sodium caffeine benzoate were determined in all the test mixtures with an error not greater than 10% by means of this photonephelometric technique.

In developing the photonephelometric technique for determining caffeine in injection solutions and in complex medicinal mixtures, we had in mind the development of a technique for the rapid analysis of such medicinal forms as are produced by the pharmaceutical industry, and for the analysis of raw materials, and finished products.

SUMMARY

1. A photonephelometric method has been developed for determining caffeine in plant material (sample weight 1 g). Experimental error is 3-5%).

2. A technique is outlined for the photonephelometric determination of caffeine in 10 and 20% solutions of sodium caffeine benzoate, which is issued by the pharmaceutical industry in ampoules, and for the determination of caffeine in medicinal mixtures containing caffeine (0.05) or sodium caffeine benzoate (0.1).

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QUANTITATIVE DETERMINATION OF REDUCING SUGARS BY MEANS OF COPPER TRIHYDROXYGLUTARATE

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The capacity of monosaccharides and some disaccharides to reduce divalent copper to the univalent state in alkaline media, has been used for their qualitative and quantitative determination. In order to prevent deposition of cupric hydroxide, it is essential that materials which combine with Cu^{2+} to give a soluble complex be present. In Trommer's test this part is played by the monosaccharide itself. Various α-hydroxy acids (tartaric, lactic, citric, salicylic [1], and trihydroxyglutaric acids [2]) are, however, used more frequently for complexing Cu^{2+}. The method most widely used at present for determination of reducing sugars is that based on the use of Fehling's solution.

When this method is used, however, a number of difficulties arise. When reducing sugars are heated in a strongly alkaline medium, they undergo fundamental changes [3], as a result of which numerous products are formed,* some of which possess reducing properties. Consequently, the amount of cuprous oxide which deposits from solution depends, not only on the amount of monosaccharides, but also on the experimental conditions used. In order to get reproducible results in the well known methods of Soxhlet [5], Allihn [6], and Bertrand [7] and in some other methods, the specified experimental conditions must be strictly adhered to, such conditions including the volume of alkali, volume of test mixture, and duration of heating. Another complication which occurs during the quantitative determination of reducing mono- and disaccharides is the fact that the Fehling's solution itself, under the experimental conditions, gives a precipitate of cuprous oxide, so that even when the specified experimental conditions are rigorously followed, there is no direct proportionality between the amount of sugar (glucose for example) and the amount of precipitated cuprous oxide, consequently, empirical tables have to be used. Some research workers have tried to eliminate the drawbacks inherent in the use of Fehling's solution by replacing tartaric acid with other organic materials containing hydroxyl groups which give soluble complexes with divalent copper; such materials include glycerol or acids – citric and salicylic.

During work with copper xylotrihydroxyglutarate we found that it readily dissolves in alkalis, and these alkali solutions do not deposit cuprous oxide even on storing for six months; consequently, they are considerably more stable than Fehling's solution which deposits a precipitate as soon as the third day.

Killani [8] has pointed out xylotrihydroxyglutaric acid does not reduce Fehling's solution.

Results are given in the present article of determinations of glucose, fructose, and maltose in which copper trihydroxyglutarate was used.

The experimental results obtained demonstrated clearly an important advantage of trihydroxyglutaric acid over tartaric acid, namely, that under strictly defined conditions, the amount of cuprous oxide deposited is proportional to the amount of sugar (glucose, fructose or maltose, respectively).

Thus, the amount of sugar (x mg) can be readily found from the formula $x = km$, where $\underline{m}$ is the amount of copper in milligrams in the cuprous oxide deposited, while $\underline{k}$ is a coefficient which has the following values, when the conditions given below are used: for glucose – 0.6068; for fructose – 0.6027; for maltose – 0.9383.

It should be added that at present trihydroxyglutaric acid is readily available, as it is prepared in large quantities by the hydrolysis industry [9].

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* According to Nef's results, up to 116 different products can be formed from hexose [4].

EXPERIMENTAL

The trihydroxyglutaric acid used in our work was the product of the Fergansky Hydrolysis Factory. The technical product was purified by the method layed down in the All Union Scientific Research Hydrolysis Institute: this consisted of the following.

A 40% solution of trihydroxyglutaric acid was prepared and allowed to stand for 24 hours in order to deposit mucic acid. 2-3% by weight of active charcoal was added to the filtrate, and the mixture heated on a water bath to a state where the refractive index of the liquid obtained was $n^{20°} = 1.4064$. It was then left for 24 hours to deposit gypsum, mucic acid, and charcoal. After the precipitate had been sucked off, the filtrate was evaporated with 5 ml of concentrated hydrochloric acid on a water bath until the refractive index was $n^{20°} = 1.4399$. After 12 hours, crystals in the form of parallelograms deposited from the solution; these were filtered off under suction, they were then washed with ethanol and dried at 60°. The yield of pure product was 80%.

The acid obtained did not rotate the polarization plane, and, after recrystallization from acetone, had a melting point of 150% (E. Fischer [10] for a product recrystallized from ethyl acetate gives a melting point of 152°).

The solution of the copper complex was prepared so that its contents of trihydroxyglutarate, alkali, and cupric sulfate, were equivalent to the Fehling's solution prepared according to Bertrand [7]; the composition was as follows:

Solution No. 1. 40 g $CuSO_4 \cdot 5H_2O$ was dissolved in water and the volume made up to 1 liter.

Solution No. 2. 128 g of trihydroxyglutaric acid and 207 g of sodium hydroxide were dissolved in water and the volume made up to 1 liter.

For sugar determination, 20 ml of Solution No. 1, 20 ml of Solution No. 2, and 20-n, ml of water were used (where n is the volume of the sugar solution in milliliters).

The copper-alkali solution prepared on the basis of trihydroxyglutaric acid is more stable than Fehling's solution on heating. This is evident from parallel blank tests whose results are given in Table 1.

TABLE 1

Experiment number	Duration of boiling, in minutes	Amount of copper deposited, in mg	
		Solution containing trihydroxyglutaric acid	Solution containing tartaric acid
1	3	–	–
2	5	–	1.29
3	10	2.51	4.10
4	15	3.87	5.16

Special tests showed that during sugar determination, the duration of boiling affects the amount of cuprous oxide deposited.

The technique which we recommend for the determination of sugars does not differ from that given in Bertrand's article [7].

n-mls of sugar solution and 20-n mls of water were introduced into a 150 ml conical flask. To this was added 40-ml of the solution of the copper complex of trihydroxyglutaric acid, obtained by pouring together 20 ml of Solution No. 1 and 20 ml of Solution No. 2. The mixture was shaken up and the clear blue liquid rapidly heated to the boiling point, after which it was boiled for exactly 3 minutes. The precipitated cuprous oxide was washed with hot, freshly boiled water, and transferred onto a No. 4 glass filter, on which it was again washed with water until the wash liquor gave no trace of an alkaline reaction; it was then dissolved in iron ammonium alum (containing 86 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ and 108 ml of concentrated sulfuric acid in 1 liter of solution). Flask and filter were washed a few times with small portions of cold freshly boiled water until there was no acid reaction. The ferrous salt formed was titrated with 0.1 N permanganate.

Determination of Glucose

A solution containing 5.00 mg of glucose per ml was prepared. The solution was standardized according to Bertrand's method.

Results of these determinations are given in Table 2.

TABLE 2

Test number	Glucose taken, in mg a	Copper found, in mg, m	Ratios of mgs of glucose to mgs of copper, k	Glucose found average value, in mg, $\bar{x}$	Dispersion, s^2	Accuracy $t_{0.95} \cdot s_{\bar{x}}$	Probable relative error, $\frac{s_{\bar{x}} t_{0.95}}{a} \cdot 100$
1	2	3	4	5	6	7	8
1—4	25.0	41.14—41.27	0.6061	24.985	$11 \cdot 10^{-4}$	0.053	0.21%
5—13	50.0	82.24—82.49	0.6073	50.006	$24 \cdot 10^{-4}$	0.038	0.08%
14—17	75.0	123.5—123.6	0.6071	75.015	$8 \cdot 10^{-4}$	0.045	0.06%

In each series of tests, the coefficient equal to the ratio of the number of milligrams of glucose to the number of milligrams of copper, was determined by the method of least squares. Column 5 contains the mean values of the number of milligrams of glucose found by means of the coefficient from Column 4. The values in Column 6 are those of the dispersion.

$$s^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1},$$

where n is the number of independent determinations.

The coefficients differed very little from each other in three series of experiments. The method therefore does not contain a systematic error.

For a final determination of the coefficient, 31 independent determinations of glucose were carried out, the amount of glucose in solution varying from 5 to 85 mg. The number of milligrams of glucose (x) in the test solution is given by:

$$x = 0.6068\ m, \tag{1}$$

where m denotes the number of milligrams of copper in the cuprous oxide.

Statistical treatment of the results by the method recommended by N. P. Komar [11], gave the following results: mean value $\bar{z} = x_i/a_i$, the relation between the amount of glucose x_i calculated by means of Formula (1) and the amount of glucose a_i taken for the determination is equal to $1.0000\ s^2 = 7 \times 10^{-6}$.

Determination of Fructose and Maltose

A fructose solution was prepared by dissolving 1.0000 g of fructose (chemically pure grade from the de Khaen factory) in water and making the volume up to 200 ml. The maltose solution was prepared by dissolving 1.2500 g of maltose (bacteriological grade) in water and making up the volume of the solution to 250 ml. Three determinations of maltose by Bertrand's method gave an average titer of 4.78 mg per ml of solution.

Results for the fructose and maltose determinations are given in Tables 3 and 4.

Here, as in the case of glucose determinations, there was observed a satisfactory proportionality between the amount of copper determined by titration with permanganate, and the amount of fructose or maltose respectively.

TABLE 3

Test number	Fructose taken, in mg, a	Copper found, in mg, m	Ratio of mgs of fructose to mgs of copper, k	Fructose found, average value, $\overline{x}$, in mg	Dispersion s^2	Accuracy $t_{0.95} \cdot S_{\overline{x}}$	Probable relative error, $\frac{S_{\overline{x}} \cdot t_{0.95}}{a} \cdot 100$
1—3	25.0	41.46—41.59	0.6019	25.000	$12 \cdot 10^{-4}$	0.086	0.34%
4—6	50.0	82.85—83.10	0.6030	50.0067	$65 \cdot 10^{-4}$	0.20	0.40%
7—9	75.0	124.3—124.5	0.6026	74.983	$43 \cdot 10^{-4}$	0.16	0.22%

TABLE 4

Test number	Maltose taken, in mg, a	Copper found, in mg, m	Ratio of mgs of maltose to mgs of copper, k	Maltose found, average value, in mg $\overline{x}$	Dispersion s^2	Accuracy $t_{0.95} \cdot s_{\overline{x}}$	Probable relative error $\frac{s_{\overline{x}} \cdot t_{0.95}}{a} \cdot 100$
1—3	23.9	25.42—25.61	0.9378	23.893	$120 \cdot 10^{-4}$	0.27	1.14%
4—6	47.8	50.95—51.16	0.9358	47.770	$100 \cdot 10^{-4}$	0.25	0.52%
7—9	71.7	76.19—76.38	0.9393	71.683	$96 \cdot 10^{-4}$	0.24	0.34%

From the results obtained during 9 independent determinations of fructose (or maltose), the following equations were derived: for fructose $x = 0.6027\ m$ (2) and for maltose $x = 0.9383\ m$ (3).

Statistical treatment of the data obtained gave the following results: average value $\overline{z} = x_i/a_i$, the ratios between the amounts of fructose and maltose calculated by means of Formulas (2) and (3) respectively, and the amounts actually taken a_i, are 1.0004 and 0.9997; $s^2 = 2 \times 10^{-6}$ and 11×10^{-6}.

The authors would like to thank N. V. Chalov for his gift of trihydroxyglutaric acid.

SUMMARY

1. A new method is suggested for determining reducing sugars by means of copper trihydroxyglutarate.

2. It has been shown that this method has the advantage over methods based on the use of Fehling's solution, that when this new method is used there is a strict proportionality between the amount of cuprous oxide and the amount of sugar.

3. It is possible, by using this method, to determine glucose, fructose, and maltose with a high degree of accuracy.

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TURBIDIMETRIC DETERMINATION OF SMALL AMOUNTS OF XANTHOGENATE AND CARBON DISULFIDE*

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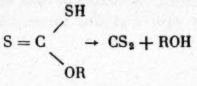
During the synthesis of xanthogenates, and during their application as flotation reagents, xanthogenate falls as dust or micro-drops of an aqueous solution, in the air of industrial establishments, while carbon disulfide forms as one of the decomposition products of xanthogenates. Methods are described below for the determination of these materials in air.

The Stability of Dilute Solutions of Potassium Xanthogenates

Turbidimetric analysis requires the preparation of stable, standard solutions of xanthogenate.

Well dried potassium xanthogenates of a high degree of purity are very stable; thus, ethylxanthogenate, 8 years after its preparation, did not contain sulfide and thiocarbonate; the content of the active material decreased during this period from 99.6 to 99.2%. The breakdown rate of ethylxanthogenate in aqueous solutions is relatively high, although it is known that the xanthogenate ion itself is fairly stable [1, 2]. With decreasing xanthogenate concentration, the stability of its solutions increases (Fig. 1). Our results are in good agreement with ideas regarding the process of spontaneous decomposition of xanthogenic acid:



$$\mathrm{S=C}\begin{matrix}\diagup\mathrm{SH}\\ \diagdown\mathrm{OR}\end{matrix}\rightarrow \mathrm{CS_2+ROH}$$

which speeds up with increasing concentration [3].

We have made a study of changes in concentration of solutions of chemically pure C_2H_5OCSSK, and of chemically pure and technical C_4H_9OCSSK with time (Fig. 1). Xanthogenate content was determined microcolorimetrically [4], and turbidimetrically; the results showed good agreement in the case of solutions of pure preparations. The alkali content was determined at the same time by titration with acetic acid using phenolphthalein as indicator.

On the basis of these experiments the following conclusions can be drawn.

1. The stability of the solutions decreases with increasing concentrations of the xanthogenates (Fig. 1 and 2, Table 1).

2. On comparing the behavior of identical solutions, prepared in different ways – one prepared by dissolving an aliquot of test material in a known volume while the second was prepared by a tenfold dilution of a concentrated solution – it was found that the first solution was the more stable of the two. It follows from this that it is necessary to dissolve the aliquot of xanthogenate in small amounts in the total volume of solvent, thereby avoiding local increases in concentration.

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* F. P. Gulyaeva took part in the experimental work.

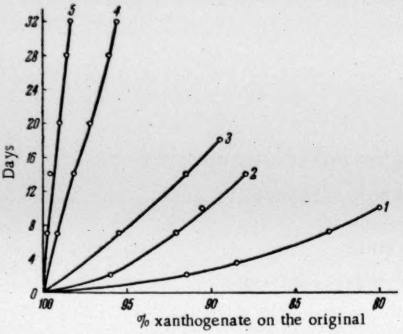

Fig. 1. The effect of the concentration of alkalinity of the medium on the stability of solutions of xanthogenates:
1) C_2H_5OCSSK 2.1 mg/ml; 2) C_2H_5OCSSK 0.21 mg/ml; 3) C_2H_5OCSSK 0.21 mg/ml in 0.001 N KOH; 4) C_2H_5OCSSK 0.21 mg/ml in 0.1 N KOH; 5) 0.25 mg/ml C_4H_9OCSSK in 0.1 N KOH.

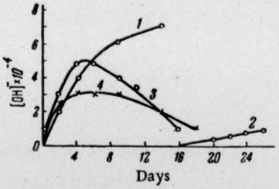

Fig. 2. Changes in the alkalinity of solutions of xanthogenates:
1) C_2H_5OCSSK 2.1 mg/ml; 2) C_2H_5OCSSK 0.21 mg/ml; 3) C_2H_5OCSSK 2.1 mg/ml in 0.001 N KOH; 4) C_2H_5OCSSK 0.21 mg/ml in 0.001 N KOH.

3. pH is of paramount importance for stabilization of the solutions of xanthogenates. The stability of the solution increases with increasing pH; this is a consequence of the depression of hydrolysis of xanthogenate and subsequent decomposition of xanthogenic acid. The results given on Fig. 2 and in Table 1, however, indicate that different processes occur at the same time. While solutions prepared in water alone show a continuous increase in alkalinity, in weakly alkaline solutions (0.001-0.01 N) there is initially an increase in alkalinity, afterwards, when a maximum value has been reached, the alkalinity drops again; in some instances the pH drops to < 9. In strongly alkaline solutions there is observed an immediate drop in the amount of titratable alkali. Such behavior of the solutions is determined by the capacity of the xanthogenates to react with alkali [5-7]. For stabilizing solutions of low concentrations, the optimum pH is approximately 13. Solutions of 0.21 mg/ml of C_2H_5OCSSK in 0.1 N KOH still retained 96% of the active material after 30 days; a similar solution of butylxanthogenate was 98% active after the same length of time.

TABLE 1

Alkalinity of Stabilized Solutions of Xanthogenates

Age of the solution, in days	Amount of 0.1 N CH_3COOH used for titrating 10 ml of solution, in ml		
	0.21 mg C_2H_5OCSSK/ml in 0.01 N KOH	0.25 mg C_4H_9OCSSK/ml in 0.1 N KOH	0.25 mg C_4H_9OCSSK/ml in 0.1 N KOH
0	0.85	9.80	11.20
3	0.90	9.80	11.20
8	0.90	9.80	11.20
13	0.85	9.80	11.20
18	0.80	9.85	11.10
25	–	9.90	11.00
32		9.85	11.00
39		9.75	11.00
46		9.70	10.9

4. From a comparison of Fig. 1 with Fig. 2 and Table 1, it is obvious that attainment of stable concentrations of a xanthogenate is accompanied by stabilization of the amount of titratable alkali.

Turbidimetric Determination of Xanthogenates

Many heavy metal xanthogenates are only sparingly soluble [8]. Pilipenko [9] qualitatively established a solubility series for the ethylxanthogenates of certain metals, and established that the solubility product of $C_2H_5OCSSAg$ is equal to 3.51×10^{-17}. Kakovsky [10] has determined the solubility product of a large number of xanthogenates, in particular, the following:

$$L_{pC_2H_5OCSSCu} = 5.2\cdot10^{-20} L_{pC_4H_9OCSSCu} = 4.7\cdot10^{-20},$$

$$L_{p(C_2H_5OCSS)_2Hg} = 1.55\cdot10^{-38} L_{p(C_4H_9OCSS)_2Hg} = 1.1\cdot10^{-40}.$$

During a study of suspensions of the xanthogenates of Fe^{3+}, Ni^{2+}, Co^{2+}, Ag^{+}, Cu^{2+}, Pb^{2+}, Hg^{2+} and Zn^{2+} (pH from 3.5-6.8), it has been found that for the turbidimetric determination of the xanthogenates of the alkali metals, the most suitable compounds are those of copper and mercury.

TABLE 2

Effect of Acetate Concentration on the Light Absorption of Suspensions of Mercury Ethylxanthogenate

C_2H_5OCSSK taken, in mg	CH_3COOK added, in mg	No. of scale readings of the galvanometer	pH of the suspension
0.105	50	64	3.31
0.105	100	67	3.40
0.105	120	66	3.46
0.105	150	68	3.55
0.105	100	70	3.64
0.210	50	38	3.40
0.210	100	39	3.48
0.210	120	37	3.58
0.210	150	36	3.68
0.210	200	40	3.83

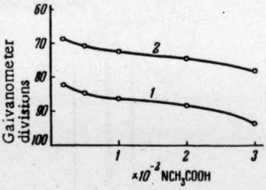

Fig. 3. Effect of acetic acid concentration on the light absorption of copper ethylxanthogenate suspensions: 1) 0.04 mg C_2H_5OCSSK; 2) 0.10 mg of C_2H_5OCSSK.

On mixing Cu^{2+} with a solution of xanthogenate there is formed a yellow turbidity of cuprous xanthogenate and dixanthogene: $2Cu^{2+} + 4SCSOR \rightarrow Cu_2(SCSOR)_2 + (SCSOR)_2$.

The turbidity can be detected visually starting at 0.02 mg of ethyl- and butylxanthogenate in 11 ml.

In order to obtain as much as possible of a monodisperse system, and exclude formation of basic copper salts, the pH should be 3.5-4.5. This is achieved by adding 0.5 ml of 0.1 N acetic acid after neutralization of the solution to the phenolphthalein end point. In the course of 15-20 minutes the light absorption increases to a maximum, afterwards, for an hour, it remains practically unchanged. Higher pH values, although they increase the stability of the turbidity as a result of an increase in the degree of dispersion of the particles, nevertheless, at the same time, lower the sensitivity of the method and slow down suspension formation. For an acetate content of more than 30 mg CH_3COOK, further increases have no appreciable effect on the optical density; this is, probably, the result of an increase in buffer capacity.

Addition of sulfates (up to 0.5 g) does not lead to an appreciable change in the dispersion of the precipitates, chlorides on the other hand, decrease light absorption, this being particularly noticeable at low xanthogenate concentrations (0.02-0.5 mg).

Mercury xanthogenates form white, very stable suspensions. The conditions used for turbidimetric determination retain the basic features of the technique using copper xanthogenate. The reaction sensitivity is somewhat higher, and the slope of the curve on the lower part is steeper than in the case of copper xanthogenate. Equimolar concentrations of the ethyl and butyl compounds give practically equal effects. At low xanthogenate concentrations, at pH 2-2.5, the optical density increases slowly and reaches a maximum after 60-75 minutes. With increasing pH, light absorption increases, and the rate at which it reaches its maximum value increases; at the same time, however, the stability of the suspension becomes low. The most suitable pH range is 3.2-4.0. Under these conditions, maximum light absorption is reached – depending on the concentration – in 30-45 minutes and keeps steady for 1-3 hours.

Salts weaken light absorption of suspensions of mercury xanthogenate to a greater extent than that of copper xanthogenate suspensions. The amount of acetate added must be strictly controlled.

In analytical practice both methods used for turbidimetric determination give similar results.

Determination of Carbon Disulfide

Experiments were carried out on the setup shown on Fig. 4. An ampoule containing freshly distilled carbon disulfide was placed in flask 1. The flask was connected in series to a buffer flask 2 and a receiver 3, packed with cotton wool, and to absorption apparatus containing an alcoholic alkali solution. While air was being slowly drawn through the system, the flask with the ampoule was stoppered with a ground glass stopper; the latter was in the form of a rod so that at the point when the flask was effectively sealed the tip of the rod broke the ampoule, and a mixture of air and carbon disulfide vapor was drawn into the absorption apparatus. The solution obtained was diluted to a definite volume and an aliquot of this final solution determined turbidimetrically. A solution with a concentration of 3% of alkali in ethanol was sufficient for complete absorption of carbon disulfide and formation of the xanthogenate. Further, the concentration is low enough to exclude the occurrence of side reactions between carbon disulfide, xanthogenate and alkali.

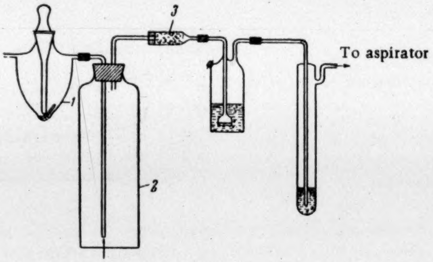

Fig. 4. General appearance of the setup.

TABLE 3

Balance for Determination of Carbon Disulfide Turbidimetrically

Weight of CS_2 taken, in mg	CS_2 found turbidimetrically, in mg			Difference, in %
	in one absorber fitted with a No. 1 porous plate	in second absorber	in third absorber	
16.2	16.0	0.40	0.00	+1.2
12.0	11.2	0.40	0.00	−3.4
6.4	6.0	0.10	0.00	−4.7
3.4	3.1	0.00	0.00	−8.9
7.3	6.85	0.50	0.00	+0.6

Most determinations gave an error not exceeding 5%. The filter does not hold back the carbon disulfide from the air stream. Dusts of technical xanthogenates are readily held by the cotton wool filter: in the course of 30 minutes, 50 mg of butylxanthogenate only gave 0.01-0.03 mg of CS_2 during passage of air with a moisture content of 60%. The necessary alkali stabilization of the xanthogenate occurs in the drop-liquid phase.

Practice has shown that xanthogenates occurring in the air of the places where they are made, do not contain sulfides and mercaptides in such amounts as would interfere with turbidimetric analysis.

SUMMARY

1. Conditions have been established for the preparation of stable solutions of xanthogenates for standard suspensions. It has been shown that the stability of xanthogenate solutions increases with decreasing xanthogenate concentration.

2. Two variants of a turbidimetric method of determining xanthogenates have been developed; they are based on measurement of light absorption by copper and mercury xanthogenate suspensions.

3. It has been demonstrated that it is possible to carry out a turbidimetric determination of carbon disulfide as xanthogenate, after absorption of the carbon disulfide by 3% alcoholic alkali.

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* In Russian.

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BRIEF COMMUNICATIONS

QUALITATIVE DETECTION OF CN^- IONS

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Chemically pure, finely ground Al_2O_3, is mixed with pure benzidene in the proportion of 1 part of benzidene to 20 parts of Al_2O_3. This mixture is closely packed into a glass tube 40 mm long and 6 mm in diameter, so that a column about 20 mm long is obtained.

The copper acetate required for the reaction is prepared as follows: 100 ml of a 1% solution of $(CH_3COO)_2$ Cu $\cdot 2H_2O$ is mixed with 5 ml of 5% CH_3COOH.

When the volume of CH_3COOH was increased, unsatisfactory results were obtained during detection of CN^- ions. Poor results were also obtained when more dilute solutions of $(CH_3COO)_2 \cdot Cu$ were used.

The solutions are introduced onto the column in the following order: 0.05 ml of the copper acetate – acetic acid solution, followed by 0.05 ml of the solution to be tested for CN^- ions.

A blue color appears in the column a few seconds after addition of the solutions. The limit of identification is $0.15\,\gamma$ of CN^-. The sensitivity of the benzidene reaction for CN^- is considerably higher when this technique is used, than when the classical method of carrying it out is employed.

Cl^-, Br^-, I^-, and SCN^- also gives reactions with benzidene. Nevertheless, if the adsorbent in the column is moistened with 95% ethanol before introducing the reagents in the order given above, CN^- ions ($1\ \gamma$) can still be detected in the presence of Cl^-, Br^-, and I^-.

SUMMARY

A method is described for increasing the sensitivity of detection of CN^- by means of benzidene and copper acetate.

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CONDUCTOMETRIC DETERMINATION OF ALUMINUM

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Aluminum ions form a stable complex with oxalate ions and calcium does not precipitate the oxalate ions from this complex. This reaction has been used as the basis of an indirect method of determining aluminum. 5 ml of a standard solution of sodium oxalate is measured into the vessel used for conductometric titration; this is followed by a known volume of test solution containing aluminum ions. 0.5 ml of a saturated solution of Methyl Violet is then added, and some well washed, dry, calcium oxalate which has been ground up in a mortar also introduced into the solution which is made up with distilled water to a volume of 30 ml.* The solution is carefully mixed and excess sodium oxalate titrated conductometrically with calcium nitrate of known concentration. If sufficient calcium oxalate and Methyl Violet have been added to the solution before commencing titration, the electrical conductivity of the solution should not change during the period following upon the addition of reagent.

The titration curve is in the shape of an ⌋.

The 0.05 N solution of sodium oxalate was standardized by conductometric titration with calcium nitrate in the presence of Methyl Violet and calcium oxalate precipitate.

TABLE 1

Determination of Aluminum Conductometrically in the Absence of Other Ions

Al^{3+} taken, in mg	Al^{3+} found, in mg	Error, in %
0.901	0.899	0.23
0.689	0.690	0.14
0.477	0.477	0
0.265	0.266	0.35
0.159	0.158	0.63
0.053	0.054	1.88
0.026	0.030	15.38

Titration was carried out on a conductometric titration setup of the Toropov type [1] in a vessel fitted with a cylindrical piston stirrer [2]. The reagent was added by means of a pneumatic micro-buret [3].

Aluminum was determined in pure solutions, and in the presence of trivalent iron ions. It follows from Table 1 that aluminum in amounts greater than 0.05 mg can be determined fairly accurately in 30 ml of test solution; when smaller amounts of aluminum are determined, the experimental error increases sharply.

Ferric ions interfere with aluminum determination since they give a complex compound. Iron ions were removed from the test solution by slight modifications of the thiosulfate method of Datsenko and Usatenko [4]. This was accomplished by adding distilled water to the test solution containing aluminum and iron ions until the volume was 20 ml, one drop of Methyl Red was then added, followed by concentrated ammonia dropwise, with stirring, until the solution acquired a yellow color.**

Concentrated hydrochloric acid was then added to the solution dropwise with shaking, until the turbidity which had appeared dissolved; one drop in excess of acid was then added followed by 2 ml of 20% sodium thiosulfate. The solution was heated to the boiling point and 1 ml of 20% ammonium acetate added, after which the solution was boiled for 2-3 minutes, and the precipitate filtered through a small loose filter. The filter was washed with hot 5% ammonium nitrate solution until the filtrate gave a negative reaction for chloride ions when it was washed three times with hot distilled water. The precipitate was transferred from the filter into a small beaker, and covered with 5 ml of 0.5 N acetic acid; it was then broken up into small pieces with a glass rod. The solution in the beaker was boiled until the sulfur had coagulated into lumps, it was then filtered into a clean beaker through a small dense filter of cotton wool, and the filter was washed three times with hot 1% acetic acetic acid. To this solution was added 1-2 drops of a 5% alcoholic solution of iodine, excess of the latter being removed by boiling. The solution thus obtained was cooled to room temperature and quantitatively transferred to the vessel used for titration, in which a known volume (5 ml) of sodium oxalate, 0.5 ml of a saturated solution of Methyl Violet, and some calcium oxalate precipitate had been placed beforehand. The solution was made up to 30 ml with distilled water, it was then thoroughly mixed and the excess sodium oxalate conductometrically titrated with calcium nitrate. From the results obtained. aluminum content of the test sample was then determined.

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* The Methyl Violet is added to prevent adsorption of ions on the precipitate which settles out; calcium oxalate is added to improve crystallization conditions.

** Ammonia is added when the test solution has an acid reaction.

When the solution was prepared in this way, good results were obtained for the determination of aluminum in the presence of large amounts (one hundred times as much) of iron. It should be pointed out, however, that in the case of small amounts of aluminum (less than 0.3 mg in 30 ml of solution) we could not get good results for the determination of aluminum in the presence of iron.

The technique described was used for determination of aluminum in aluminum metal. For this purpose an aliquot of aluminum metal (technical aluminum dust, chippings, shavings, sheet aluminum) weighing about 1 g was dissolved in hydrochloric acid (1 : 1). The solution was filtered (when the solution obtained was turbid) into a 200 ml standard flask, the filter was washed a few times with distilled water and the solution finally made up to the mark. After thorough mixing, known volumes of the solution thus prepared were measured out for determination of aluminum by the ammonia method (Kolthoff's method) and by the technique suggested above.* Iron was tested for by reaction of test solution with potassium ferrocyanide.

TABLE 2

Determination of Aluminum in Metallic Aluminum

Sample number	Found, in %	
	By the ammonia method	Conductometrically
1	99.40	99.78
2	98.44	99.15
3	96.65	97.72
4	93.18	93.72
5	91.30	92.72

Aluminum was separated from iron by means of potassium hydroxide when the ammonia method was used for its determination. The method suggested, on the basis of the results given in Table 2, can be used for analysis of aluminum metal for aluminum.

The fact that the aluminum content as determined by the ammonia method is lower than that determined by the conductometric method, can, presumably, be explained by the adsorption of aluminum on the precipitate of ferric hydroxide during removal of aluminum from iron by means of potassium hydroxide.

SUMMARY

A conductometric method has been developed for the determination of aluminum in solutions containing ferric iron. The method can be used for the determination of aluminum in various samples of aluminum metal.

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* For determination of aluminum by the method suggested, the solution thus prepared was diluted 10 times.

TITRIMETRIC DETERMINATION OF FLUORIDE IN NATURAL WATERS*

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Methods for the direct titration of fluorides by means of thorium nitrate, using Alizarin S (sodium 1,2-dihydroxyanthraquinone sulfonate) as indicator, have been described several times in the literature [1].

According to experiments which we have carried out, the optimum acidity for titration of fluorides with thorium nitrate lies at pH 2.0-2.3, and not at 3.0 as indicated in the literature. Within this pH range, thorium nitrate is used up in amounts which are exactly proportional to the fluoride concentration of the test sample of water, and the titration results show good reproducibility. The requisite pH value is achieved, not by addition of a buffer mixture, but by addition of the calculated amount of 0.1 N HCl to the test water. In order to maintain the pH of the solution during titration, the thorium nitrate is also acidified with hydrochloric acid to the required pH.

In order to remove the deleterious effect of sulfates on the formation of the alizarin-thorium lake, calcium or magnesium chloride should be added to the solution being titrated. Barium chloride cannot be used. Calcium chloride inhibits the sulfate effect most effectively at pH 2.45-2.60. In more acid solutions, the effect of the calcium chloride is somewhat weakened, while in more alkaline solutions aluminum and iron start to interfere strongly. Practically complete suppression of sulfates is, however, only observed at sulfate concentrations of the test water not in excess of 100-120 mg/liter. At higher sulfate concentrations it is necessary to dilute the test water before titration, by addition of distilled water.

Ferrous compounds in concentrations normally met in natural waters do not interfere with fluoride determination, since Fe^{2+} ions do not form stable compounds with either fluoride ions or with Alizarin S. Ferric ions do not interfere as long as their concentration in the test water is less than 0.2 mg/liter. At higher concentrations (up to about 1.0 mg/liter) the effect of ferric ions can be eliminated by reducing ferric to ferrous ions beforehand by means of hydroxylamine. For this purpose, about 20 drops of a 5% solution of hydroxylamine is added to 50.0 ml of test water, and the solution then heated to 80-90°. After cooling, the reagents are added as indicated below, and the solution titrated with thorium nitrate.

No other components present in natural waters interfere with fluoride determination.

Reagents. The following reagents are necessary for direct titration of fluoride.

1) Thorium Nitrate Solution. 0.200 g of anhydrous $Th(NO_3)_4$ is dissolved in 700-800 ml of distilled water in liter standard flask. 70.0 ml of 0.1 N HCl is added to the solution and the volume made up to the mark with water.

2) Indicator Solution. 0.100 g of Alizarin S is dissolved in 10.0 ml of 0.1 N NaOH (or KOH) and diluted to 100.0 ml with distilled water.

3) Sodium Fluoride (or NH_4F) Solution, containing 0.020 mg F/ml; these solutions are prepared from chemically pure grade NaF (or NH_4F).

4) Saturated Calcium Chloride Solution, prepared from chemically pure $CaCl_2 \cdot 6H_2O$ free from fluoride.

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* The experimental part was carried out by E. V. Nekrasova.

5) Exactly 0.1 N HCl, free from iron and fluoride.

Standardization of Thorium Nitrate Solution. Into two similar 100 ml conical flasks, made of colorless glass, was introduced 50.0 ml of distilled water, and 1.0 ml each of a saturated calcium chloride solution and indicator solution; the whole was thoroughly mixed and then neutralized with 0.1 N HCl until the raspberry color changed to a lemon yellow, after which, to each flask was added 2.5 ml of exactly 0.1 N HCl. To the first flask was then added, dropwise, and with constant agitation, 0.80 ml of thorium nitrate, while to the second 0.90 ml of thorium nitrate solution was added (ΔV).

Alizarin thorium lakes were formed in these two control flasks in amounts proportional to the thorium nitrate added. The control solutions do not keep for more than 6-8 hours.

NaF samples	F^-, in mg	
	added	found
In double distilled water	0.10	0.08, 0.11, 0.12
	0.20	0 22, 0.20, 0.21
	0.30	0.27, 0.31, 0.33
	0.40	0.43, 0.41, 0,37
	0.60	0.56, 0 62, 0.58
In conductivity water	0.10	0.11, 0.12, 0.10
	0.20	0.22, 0.20, 0.23
	0.30	0.31, 0.34, 0.30
	0.40	0.42, 0.38, 0.44
	0 60	0,63, 0.61, 0.64

The thorium nitrate was standardized with NaF (or NH_4F) solution. The solutions were brought together in the following order. Into a conical flask was poured 48.0 ml of distilled water, 2.0 ml of NaF solution, 1.0 ml of saturated $CaCl_2$ solution, and 1.0 ml of indicator solution. The solution was carefully neutralized with pure 0.1 N HCl to a lemon yellow color, after which another 2.50 ml of 0.1 N HCl was added.

Titration of the solutions with NaF was carried out on a background of white paper or opal glass. The thorium nitrate solution was added dropwise with constant agitation. Titration was complete when the color of the solution being titrated was similar to the color of the first or second control solution.

Let the total amount of thorium nitrate used up for titration be designated by V. From this ΔV is deducted, this representing the amount of thorium nitrate already in the control solutions. The required, true amount of thorium nitrate used up in the titration will be given by $V_x = V - \Delta V$.

Standardization was carried out in 2-3 parallel determinations.

Determination of Fluoride in Water. Fluoride was determined in natural waters in exactly the same way as the thorium nitrate solution was standardized by means of sodium fluoride. 50 ml of natural water or water which had been diluted beforehand was taken for a determination. The reagents were added in exactly the same sequence, and in exactly the same amounts as before; 2.5 ml of 0.1 N HCl was finally added, and the solution titrated with thorium nitrate solution using the control solutions containing the alizarin-thorium lake.

The method was checked (see Table) by means of solutions of NaF which were prepared in double distilled water and in conductivity water, from which fluorine had been removed by preliminary distillation with water vapor.

The method described has been used for several years for determination of fluoride in water at the former Scientific Research Sanitary Hygiene Institute, and is being used at present in the Central Chemical Laboratory of the Ural Geological Administration, and in several Hydrochemical Laboratories in the Sverdlovsk Region.

SUMMARY

The method for the direct titration of fluoride by means of thorium nitrate solution, using Alizarin S as indicator, has been improved. The method can be used for the analysis of natural waters.

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PHOTOCOLORIMETRIC DETERMINATION OF PHENOXY GROUPS IN ORGANOSILICON COMPOUNDS

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Determination of phenoxy groups in organosilicon compounds is based on hydrolytic cleavage of the phenoxy groups as phenol, and the subsequent photocolorimetric determination of the latter on the basis of the blue color of indophenol which is formed by interaction of phenol with chlorine or bromine water in the presence of NH_4OH [1, 2].

An aliquot of the test organosilicon compound was dissolved in 5-6 ml of ethanol, and 4 ml of concentrated ammonia solution was added; the mixture was heated under reflux for 3-4 minutes on a boiling water bath. The precipitate formed was filtered off and washed. The filtrate obtained, plus the wash liquors, were diluted to the mark in a standard 25 ml flask. 30 drops of chlorine or bromine water was added to the solution thus obtained and this solution then heated for 5 minutes under reflux on a boiling water bath. The solution acquired a greenish blue color. On cooling, the optical density of the solution was measured on a Pulfrich photometer.

A calibration curve was constructed by making a solution of phenol in alcohol, each milliliter of the solution containing 10 mg of phenol. Known amounts of this solution were measured out with a pipet, and transferred to flasks, and then subjected to exactly the same procedure as the aliquot of the original phenoxysilanes; the optical density of the standard solutions was then measured.

The relative experimental error for the determination of phenoxy groups in tetraphenoxysilanes was found to be 0.83%, while in the case of phenyltriphenoxysilane it was 0.27% (with chlorine water) and 0.1% (with bromine water).

SUMMARY

A quantitative method for the determination of phenoxy groups in organosilicon compounds, which is described, is based on the hydrolytic cleavage of the phenoxy group as phenol. The latter, on interaction with chlorine or bromine water in the presence of NH_4OH, forms indophenol which is then determined photocolorimetrically.

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FOR THE ATTENTION OF INSTRUCTORS OF SCIENTIFIC WORKERS IN HIGH SCHOOLS

Starting in 1957 a new journal will make its appearance, namely "Scientific Reports of High Schools" with a section on "Chemistry and Chemical Technology"; this journal will include articles containing the most important results of new studies in various fields of chemistry and chemical technology. The articles should not occupy more than 6 pages of typewritten material (with two spaces) and four diagrams.

The journal will have the following sections:

1. Physical chemistry
2. Inorganic chemistry
3. Organic chemistry
4. Analytical chemistry
5. Chemistry and technology of high molecular weight compounds
6. Chemistry and technology of silicates
7. Technology of inorganic materials
8. Technology of organic materials
9. Chemical technology of fuel
10. Process and apparatus of chemical production

The journal will be published 4 times a year, the volume of each number will be 15 printed pages.

The editorial board of the journal invites all teachers and scientific workers to take an active part in the work of the journal by publishing the results of their most important work in it.

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